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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS

ERNEST MERRITT, and FREDERICK BEDELL

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OCTOBER, 1910

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THE

PHYSICAL REVIEW.

A METHOD OF MEASUREMENT OF THE PELTIER E.M.F. IN ABSOLUTE UNITS.

By Harold C. Barker

THE measurement of the Peltier E.M.F. in absolute units has been undertaken in the past by a few investigators, who have applied various more or less refined calorimetric procedures to that end.

Le Roux[1] used a system of two calorimeters containing water or mercury, and noted the changes in temperature with mercury thermometers, estimating to 0.01°.

Jahn[2] applied the Bunsen ice calorimeter.

Lecher[3] has devised a special form of calorimeter, using petroleum as absorbent. He calibrates it by electrical heating, and measures the changes in temperature in terms of galvanometer deflection with the aid of ten iron-constantan thermo-elements in series.

Czermak,[4] using Lecher's apparatus, has determined the absolute values of certain Peltier E.M.F.'s through a wide range of temperature.

The method now to be described rests essentially upon the following principle. Given two vessels containing a suitable liquid heat absorbent, thermally equal in every respect when at a common temperature, exposed to the same external conditions, and initially

[1]Ann. de Chimie et de Physique, 4e série, T. X., p. 201. 1867.
[2]Ann. der Physik, Neue Folge, Bd. XXXIV , p 755, 1888.
[3]Sitzungsb. d. kaiserl. Akad., Wien, 115, 2a, p. 1505, 1906.
[4]Sitzungsb. d. kaiserl. Akad., Wien, 116, 2a, p. 657, 1135, 1907.

at the same temperature, the condition that they shall remain at a common though changing temperature is that heat shall be supplied to the two at equal rates.

Now if, exclusive of external sources or sinks assumed common to the two, the sources consist of a current-carrying conductor composed of dissimilar metals, say M and N, the MN junctions being all in one vessel, and the NM junctions all in the other, it is evident that owing to the reversibility of the Peltier effect, the rates at which heat is supplied to the two are different, and a difference in temperature will ensue. But, if in each vessel be also placed a suitable heating coil to which current may be supplied at will, it will plainly be possible to compensate, equalizing the rates and maintaining the two vessels at a common though increasing temperature.

Let i = current in MN conductor.
R_a = resistance of MN conductor in vessel A.
R_b = resistance of MN conductor in vessel B.
a = resistance of heater in vessel A.
b = resistance of heater in vessel B.
i_a = current in heater (a).
i_b = current in heater (b).
P = Peltier E.M.F.
n = number of junctions in each vessel.

Suppose the condition of compensation to have been attained by use of the heater in vessel B. To express the equality of the rates, we have

$$R_a i^2 + nPi = R_b i^2 - nPi + bi_b^2. \qquad (1)$$

If $R_a = R_b$ this is sufficient to determine P. But such equality is quite unnecessary. Reversing i, and again securing the compensated condition, now by the use of heater in vessel A, we have

$$R_a i^2 - nPi + ai_a^2 = R_b i^2 + nPi. \qquad (2)$$

Subtracting (2) from (1) eliminates R_a and R_b, giving

$$2nPi - ai_a^2 = -2nPi + bi_b^2.$$

Whence

$$P = \frac{ai_a^2 + bi_b^2}{4ni}.$$

It is impossible in practice to realize a condition of complete thermal equality of the two vessels. The effect of inequality must therefore be considered.

Let C_a and C_b represent the respective heat capacities of the two vessels, including contents.

Let θ, θ_1, θ_2, represent the temperature of the surrounding medium, and the common temperature of the two vessels in successive cases, respectively.

Also, let k_a and k_b represent "radiation constants" of the two vessels, in joules per degree per second, if the electrical quantities are measured in the practical system.

Now, the condition of compensation implies merely the equality of the rates of change of temperature with time for the two vessels.

That is, with the current i in the first sense, as above,

$$\frac{R_a i^2 + nPi - k_a(\theta_1 - \theta)}{C_a} = \frac{R_b i^2 - nPi + bi_b^2 - k_b(\theta_1 - \theta)}{C_b}.$$

Reversing the current

$$\frac{R_a i^2 - nPi + ai_a^2 - k_a(\theta_2 - \theta)}{C_a} = \frac{R_b i^2 + nPi - k_b(\theta_2 - \theta)}{C_b}.$$

Eliminating R_a and R_b by subtracting

$$\frac{2nPi - ai_a^2}{C_a} + \frac{k_a(\theta_2 - \theta_1)}{C_a} = \frac{-2nPi + bi_b^2}{C_b} + \frac{k_b(\theta_2 - \theta_1)}{C_b}.$$

It will now be seen that the conditions justifying the assumption

$$\frac{k_a(\theta_2 - \theta_1)}{C_a} = \frac{k_b(\theta_2 - \theta_1)}{C_b}$$

can readily be attained. The proper choice of calorimetric vessels will make k_a and k_b very small and nearly equal. Again, $\theta_2 - \theta_1$ need never be large, and is common to both members. The numerators can therefore be made small and nearly equal, and if C_a and C_b be not unreasonably different, the assumption is justified.

Making this assumption, we have

$$\frac{2nPi - ai_a^2}{C_a} = \frac{-2nPi + bi_b^2}{C_b}.$$

Whence

$$P = \frac{C_b a i_a^2 + C_a b i_b^2}{2ni(C_a + C_b)}.$$

Now C_a and C_b can be made different by a relatively small amount. Let

$$C_b = C_a + c.$$

Then

$$P = \frac{C_a\left(a i_a^2 + b i_b^2 + \frac{c}{C_a} a i_a^2\right)}{4niC_a\left(1 + \frac{c}{2C_a}\right)},$$

or

$$P = \frac{1}{4ni}\left(a i_a^2 + b i_b^2 + \frac{c}{C_a} a i_a^2\right)\left(1 + \frac{c}{2C_a}\right)^{-1}.$$

Expanding the last factor, we have

$$P = \frac{1}{4ni}\left(a i_a^2 + b i_b^2 + \frac{c}{C_a} a i_a^2\right)\left(1 - \frac{c}{2C_a} + \frac{c^2}{4C_a^2} - \frac{c^3}{8C_a^3} + \cdots\right).$$

From which

$$P = \frac{a i_a^2 + b i_b^2}{4ni} + \frac{c}{2C_a} \cdot \frac{a i_a^2 - b i_b^2}{4ni} - \frac{c^2}{4C_a^2} \cdot \frac{a i_a^2 - b i_b^2}{4ni} + \cdots,$$

or

$$P = \frac{a i_a^2 + b i_b^2}{4ni} + \frac{c}{2C_a} \cdot \frac{a i_a^2 - b i_b^2}{4ni(1 + c/2C_a)}.$$

It is hardly open to question that no difficulty will be found in making c so small that, considering also the relation between the sum and difference of the nearly equal quantities $a i_a^2$ and $b i_b^2$, no term but the first need be retained. The working formula in actual practice is thus the same as that developed on the originally stated assumptions, namely

$$P = \frac{a i_a^2 + b i_b^2}{4ni}.$$

It is to be noted that the approximate thermal equality of the two vessels is subject to easy test, by supplying the two heaters alone with measured currents simultaneously, and thus determining the relation between the rates of supply of heat to the two vessels such that no difference of temperature shall result.

The realization of the conditions outlined in the foregoing discussion was attempted with the aid of the apparatus illustrated by the diagram.

Two closely similar Dewar vacuum jacketed tubes were chosen as calorimeters. The heat absorbent finally used was paraffin oil. A copper-constantan thermo-element with one junction in each

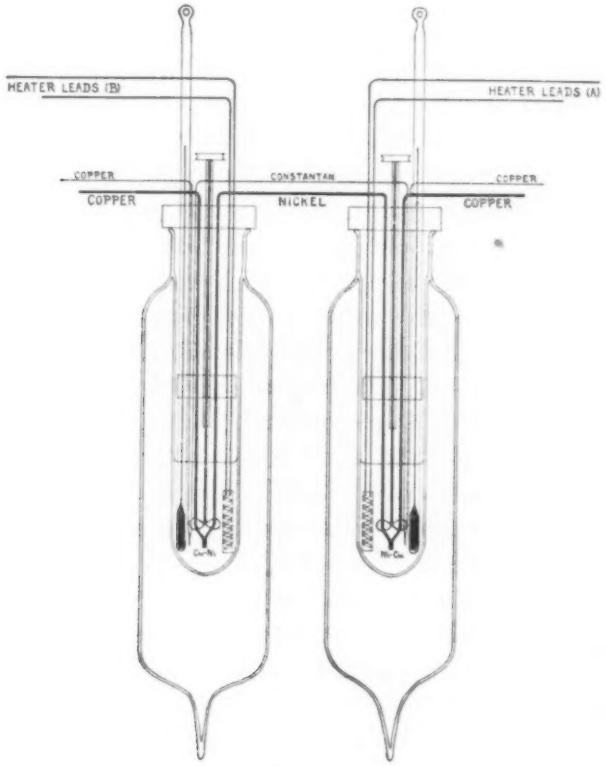

Fig. 1.

vessel served, when the circuit was closed through a D'Arsonval galvanometer of high sensibility, as an efficient differential thermometer. Each tube was provided with a mercury thermometer graduated to 0.2°, to determine the approximate temperature during the measurement.

The stirring apparatus consisted of two simple stirrers, each made of a heavy nickel wire terminating below in a small propeller blade,

and above provided with a hard-rubber pulley to receive a slender belt. A piece of glass tube supported the stirrer as indicated in the diagram. A small electric motor was used to keep the stirrers in rapid rotation throughout the experiment.

The two heaters were made of no. 38 manganin wire wound on strips of mica, with copper leads. The resistances were $a = 12.24$ and $b = 11.13$ ohms. A storage cell was used to supply the heaters, with appropriate rheostats, and a Weston milammeter to measure the current.

The subject of experiment was nickel-copper. For clearness, only one junction is shown in each tube; the actual number was five. The current was supplied by nine storage cells, three groups in parallel, each of three cells in series. This current was regulated by rheostat and measured by a shunted milammeter.

The entire system was mounted by means of two wooden disks for each tube, one at the top of greater diameter, and one within the tube and loosely fitting it, through which the wires, thermometers and stirrers pass. The two calorimeters were finally packed into a large glass jar with cotton wool.

The order of operation was simply as follows: With the current i in the first sense, the compensating current i_b was determined. The current i was then reversed, and the compensating current i_a determined. In preliminary work, the compensating current was reached by gradual approximation until a current was found that caused no deflection in some minutes. But this was quite tedious and uncertain compared with the later method, which consisted in noting the deflections each minute with currents less and greater than the compensating current by about 0.01 ampere, plotting the curves, and interpolating for the square of the compensating current between the squares of the two currents used, assuming the slope of the curve where it crossed the axis (galvanometer zero) to be a linear function of the current squared. In this manner the compensating current was determinable in an average time of about thirty minutes, during which the temperature of both calorimeters rose 1 to 3 degrees according to the value of i.

The sensibility of the differential thermometer as used is perhaps best shown by the following illustration: The average value of the

change of deflection per minute for a difference of 0.001 ampere from the compensating current, whose total value was of the order of 0.1 ampere, was 0.015 cm., the scale being distant about 165 cm. from the galvanometer, and easily readable to 0.01 cm.

The galvanometer functioned as a rule quite regularly and satisfactorily; for a time, however, preceding a breaking of the suspension, there was an erratic variation in its zero, which undoubtedly affects some of the measurements in some degree.

Some possible refinements and extensions of the adopted procedure are quite obvious. An increase in the heat capacity would make it easier to secure substantial equality, and would admit carrying out a measurement with a smaller total change in temperature, provided the differential thermometer were made more sensitive. This last end is easily attainable by using a number of thermo-elements in series in place of a single element.

It would be desirable also to surround the calorimeters with a medium whose temperature could be kept constantly equal to that of the calorimeters, thus reducing liability of error from radiation. With this precaution, the experiment could be carried out successfully at temperatures widely different from room temperature.

The subjoined table gives the results of all of the experiments made with the apparatus in the present form, none being omitted. One is incomplete, the effort to determine i_b failing by reason of serious galvanometer irregularity. P is stated in volts; it can be reduced to calories per coulomb by division by 4.19.

ai_a^2	bi_b^2	i	P	Approximate Mean Temperature.
.1684	.1724	2.448	6.96×10^{-3}	32.5°
.1730	.1669	2.444	6.95	32.5
.1397	.1353	2.028	6.78	30.0
.1157	.1040	1.620	6.78	30.0
.1137	.1017	1.612	6.68	29.5
.1723	.1642	2.436	6.91	29.0
.1015	.0987	1.521	6.58	26.5
.1431	.1303	2.036	6.71	26.0
.1424	.1278	2.034	6.64	26.0
.1026	.0951	1.522	6.49	25.0
.1421	——	2.028	——	23.0

Mean value of ten results: $P = 6.75 \times 10^{-3}$ volts at 28.7°.

Jahn's results give, at 0°, 5.08 $\times 10^{-3}$ volts; Czermak finds, at 19°, 8.04 $\times 10^{-3}$ volts.

I submit these results now with some reluctance, as I am conscious that the method has not been fully investigated; but do so in view of an enforced interruption of the work, of uncertain duration.

It is a pleasure to me gratefully to acknowledge the assistance of my friend and colleague, Dr. R. H. Hough.

The Randal Morgan Laboratory of Physics,
University of Pennsylvania.

A METHOD OF MEASURING INTENSITY OF SOUND.[1]

By W. M. Boehm.

WHILE engaged in determining the correction due to the open end of a resonator, the author found it necessary to try several of the methods devised for the purpose of measuring intensity of sound.[1] It may be of interest to note the possibilities of these methods in practical application.

The apparatus devised by Rayleigh[2] consisted of a disk preferably in the shape of an ellipse, suspended by a thread of unspun silk. The ellipse is suspended at an angle of about 45° in a cylindrical resonator which is adjusted to the proper pitch. A mirror properly mounted enables the observer to take readings with telescope and scale. In using this device it was found necessary to attach the ellipse to a small rod at the lower end of which was attached a smaller disk to be immersed in water for purposes of damping. This instrument gives very steady deflections but requires a louder sound and is somewhat sluggish if the damping is great enough to overcome the usual air-currents in a room. The method of crystal-rectifiers, as devised by Pierce,[3] was probably not given a fair trial since a limited number of crystals not the best adapted for the purpose, were at hand. There was devised another method making use of the Duddell thermo-galvanometer. At the time of writing this article there appeared in the Physical Review for April, 1910, an

[1]F. Auerbach, Coherers Affected by Sound, Ann. d. Phys. & Chem., 64, III., pp. 611–617, 1898.

W. Zernov, Absolute Measure of Sound Intensity, Ann. d. Phys., 21, IV., pp. 131–140, 1906; also Ann. d. Phys., 26, p. 79, 1908.

B. F. Sharpe, Measurement of Sound, Science, p. 808, June 9, 1899.

A. G. Webster, A Portable Apparatus for the Measurement of Sound, Science (N. S.), Vol. 17, p. 175, 1903.

[2]Lord Rayleigh, An Instrument Capable of Measuring the Intensity of Sound, Phil. Mag., Vol. 15, p. 186, 1882.

[3]G. W. Pierce, A Simple Method of Measuring the Intensity of Sound, Proc. Amer. Acad., 43, p. 375, 1908.

article by F. R. Watson[1] describing the method as devised by him. Since the method here used is practically the same, though independently devised, the reader is referred to that article for a description. It is an excellent method where the sound is moderately loud but could not be used in this case because the thermo-galvanometer is too slow in recovering from the incidental disturbances which occur several times a second in a large city.

Method of Vibration Galvanometer.—The method finally adopted is that shown diagrammatically in Fig. 1. A resonator of proper

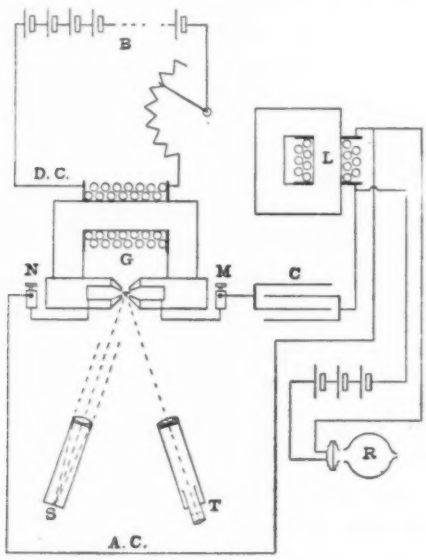

Fig. 1.

pitch, or adjustable, is placed at R, a short distance from a telephone transmitter. The deflections will be greater if the resonator is placed with the larger opening toward the transmitter. At L there is a transformer, of large self-induction and low resistance, in series with the transmitter and battery. In parallel with this is the galvanometer circuit which has a capacity in series. The image of the slit S is reflected by a small mirror attached to the vibrator. A maximum of sound at R is indicated by a maximum width of band seen through the telescope. The vibrator in the

[1]F. R. Watson, An Apparatus for Measuring Sound, PHYS. REV., Vol. XXX., p. 471, 1910.

galvanometer consisted of a number of short magnets mounted parallel, one above the other, on a sheet of mica to which was attached a very good small mirror. This strip was then attached to a phosphor-bronze galvanometer suspension of ".003 inch."

Adjustable bridges and adjustable tension give the vibrator some range but not very much. For frequencies varying by an octave, different suspensions are required.

To tune the galvanometer, disconnect the galvanometer from its circuit and connect a telephone receiver to it at *M* and *N*. Excite the poles by connecting the D.C. circuit and pluck the vibrator mechanically. Several sounds can be heard in the receiver but by adjusting the tension it is possible to distinguish the transverse from the torsional vibrations. It is possible, by this method, to tune the galvanometer to the pitch of the fork or source of sound. If necessary, sharper tuning may be attained by disconnecting the receiver, joining the galvanometer as shown in the drawing, placing the source near *R* and adjusting the tension on the vibrator until the widest band is observed in the telescope.

The above arrangement can be made very sensitive to sounds of small amplitude. For ordinary sounds it is necessary to shift the observing telescope *T* because the band becomes so wide as to go out of the field. The method is especially useful on account of the rapidity with which it responds to stimulation and recovers from vibrations of the building. Accidental vibrations are easily distinguished from steady ones. Generators or motors in the building or the blast of a locomotive may interfere sufficiently to make observations impossible but traffic along the street produced less annoyance than a person walking over the floor. Trolley cars were less annoying on account of the jarring to the ground than they were on account of a sound of high pitch produced by the motor and often reaching the pitch of the fork used in the experiments.[1]

In conclusion I wish to thank Dr. R. H. Hough, of the Randal Morgan Laboratory, for suggesting the use of the vibration galvanometer as well as coöperating in its design and construction.

RANDAL MORGAN LABORATORY,
UNIVERSITY OF PENNSYLVANIA.

[1]F. Wenner, Annalen d. Physik, 309, p. 425. See also "A Theoretical and Experimental Study of the Vibration Galvanometer," Bulletin Bureau of Standards, p. 347, May 25, 1909, or Reprint No. 134.

A DETERMINATION OF THE CORRECTION FOR THE OPEN END OF A CYLINDRICAL RESONATOR.

BY W. M. BOEHM.

DURING the past decade, several methods for measuring the intensity of sound, have been developed. Among the applications of these methods, that of the determination of the correction which must be added to the length of a cylindrical resonator, was considered worthy of re-determination.

The values of the correction which are generally quoted are those of Blaikley.[1] His values give an average of $(.576)R$ (R being the radius of the resonator) for resonators having a flange of small width. For resonators having a flange of infinite width at the open end, Rayleigh[2] has determined, by theoretical methods, that the correction is about $(.82)R$. For a flange of "zero" width, there is at present no theoretical determination.

In outline, the method used in this investigation was as follows: The source of sound was held near the open end of a cylindrical resonator the length of which was adjusted until the point of maximum resonance was found by one of the methods for measuring intensity of sound. In this way the position of one or more nodes was found. Wave-lengths and corrections were determined from the positions of these nodes. Observations were taken as rapidly as possible to avoid changes of humidity and temperature.

Resonators.—The resonators were made of drawn steel tubes, manufactured by the Seamless Tube Co., of Pittsburg. The thickness of wall was about 6.5 mm. except a distance of 50 mm. at the top which has turned to a thickness of 3.1 mm. Heavy face-plates of cast iron were finished to fit the top closely. At the lower part, the tubes were mounted firmly with set-screws having

[1]D. J. Blaikley, Experiments for Determining the Correction to be Added to the Length of a Cylindrical Resonant Tube, Phil. Mag. (V.), Vol. VII., p. 339, 1879.

[2]Lord Rayleigh, Theory of Sound, Vol. II., p. 487.

conical points. The base *C*, Fig. 1, was finished to fit the four resonators and to serve as a guide for the piston rod *G*. Into the lower part of the base there was screwed a heavy round rod *H*. It served two purposes: upon it was engraved the scale by means of which measurements were made and the table *J* could be fastened at any point to support the rack and pinion apparatus *K*. A clamp attached to *K* served as a lever to make find adjustments. of the position of the piston. Readings were taken with a vernier having a least count of .005 cm. attached to the piston-rod at *I*. The piston *E* was turned to a diameter slightly smaller than the inside diameter of the tube. In order to produce an air-tight fit, a leather washer having the diameter about 0.5 mm. larger than the tube was clamped to the upper side by means of a plate *F*. It was then forced into the tube. The excess of leather was thus cut off by the sharp inner edge of the tube and a very closely fitting piston was produced. All parts of the resonator were made massive to make the surface of the metal as nearly as possible a surface of zero kinetic energy.

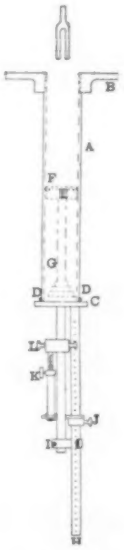

Fig. 1.

Source of Sound.—The attempt to obtain a source which would produce a sound of constant amplitude failed. Heavy tuningforks driven by electro-magnets could not be manipulated and smaller ones driven by the larger were not sufficiently constant. Organ pipes proved to be still more irregular. The most reliable source was found to be a tuning fork which vibrates freely with a gradually decreasing amplitude. In making observations through the telescope due allowance must be made for the gradual but definite change in amplitude.

Position of Node.—To determine the position of a node accurately it was necessary to use the method of measuring sound with a vibration-galvanometer.[1] The transmitter and resonator of this apparatus were placed a distance of about two meters from the resonator and either above or below the plane of the flanges. They were separated from the floor by cushions to prevent vibra-

[1]W. M. Boehm, A Method of Measuring Intensity of Sound, PHYS. REV.

tions from other sources from reaching the transmitter. The fork was struck with a hammer made of rubber and the piston moved to a position near the node. Finer adjustments were made with the rack-and-pinion apparatus while observing the vibrations of the galvanometer. Before the vibrations become inaudible, the piston can several times be gradually shifted through the point of maximum resonance. The forks used had frequencies of about 384, 768, 1,536 half-vibrations per sec.

Maxima of Intensity.—When the fork is very near the opening of the resonator, the intensity increases very sharply as the piston is moved through the proper position. See curve no. 1, Fig. 2. If the fork is farther away the increase is not so sharp, no. 2, Fig. 2. If the fork is removed still farther it is possible to find a position at which there appear to be three maxima though not very marked. The curve no. 3, Fig. 2, is exaggerated to show this peculiarity. The third maximum is less intense than the first. In curve no. 6, Fig. 4, three of these maxima are shown for a distance of about 8.4 cm. between resonator and fork. On moving the fork still farther it is found that two maxima of unequal magnitude can be obtained (see no. 4, Fig. 2). The first and more intense maximum seems to be displaced from the point where maximum resonance would be expected. The curves, roughly shown in Fig. 2, are not produced by the same amplitude of vibration, but merely represent how the intensity varies as we pass through a maximum. The middle line is also shifted to coincide for the four curves.

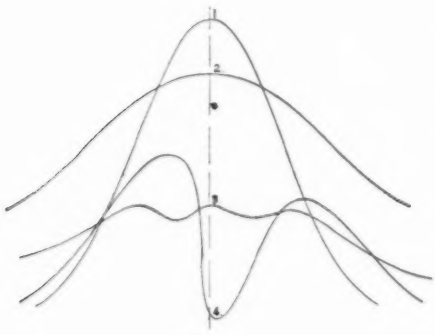

Fig. 2.

These results point to a caution. If the apparatus which is to detect the intensity of sound is outside the resonator, a maximum of intensity may not indicate "unison" between the resonator and the wave-length or frequency produced outside. This is especially true for distances greater than 8 cm. between the resonator and fork.

Distance of Fork and Position of Node.—The fork having a frequency of about 768 half-vibrations per second was placed with its prongs pointing downward parallel to the axis of the resonator. The point of maximum resonance was obtained with a fork at different distances from the resonator. The observations are shown in curve no. 1, Fig. 3. It can be seen that the position of the node

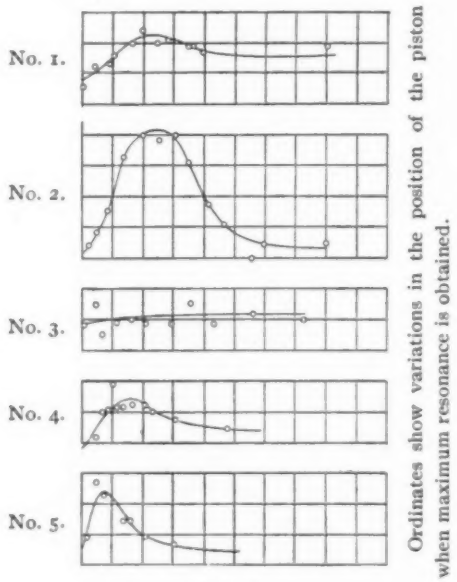

Fig. 3.

Abscissæ are proportional to distance from mouth of the resonator to the fork.

and therefore the length of the resonator varies as the distance to the fork is altered. First the resonator becomes longer until the fork is about 2.5 cm. from the opening, then it becomes shorter until it becomes apparently constant.

To ascertain this effect on a node nearer the end of the tube, the fork having a pitch an octave higher was selected. The curve obtained is shown as no. 2, Fig. 3. Using the same fork but the third node instead of the first, gave a curve which is not so marked, no. 3, Fig. 3. Resonance being very feeble, the observations do not agree so well as those for the upper node.

To ascertain the effect of width of flange upon the character of

the curve, another pipe was selected and the fork of 768 vibrations used. The curve no. 4, Fig. 3, shows the variation in position of the node when the width of flange was 0.31 cm. and no. 5 the curve when the width of flange was 13.34 cm. If these indicate anything conclusive it may be that, in the case of the larger flange, the least correction, *i. e.*, the maximum of the curve is nearer the origin or when the fork is nearer the resonator.

All curves of the upper node show a decided maximum and make it evident that an average of the observations cannot be taken as the true position of the node. A more correct value would be that obtained when the fork is a great distance from the tube. This distance would probably be about 15 to 20 cm. in the case of the fork generally used in these experiments. Since the observations become uncertain at such great distance it is necessary to assume

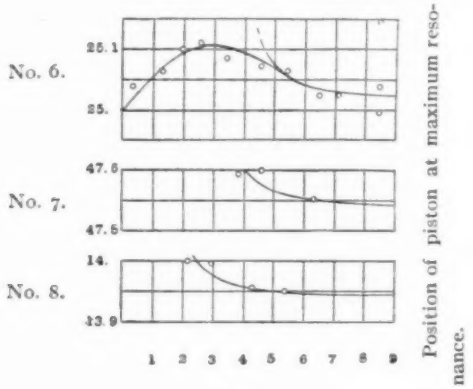

Fig. 4.

Distance from fork to resonator.

that the curve is a straight line parallel to the X-axis in this neighborhood. If, then, we select some curve which approaches an asymptote we can, by comparing it with a rather complete curve, ascertain what parts of the two curves coincide and take observations along these parts. The template at hand was that of an equilateral hyperbola which, in no. 6, Fig. 4, is shown drawn farther toward the origin to indicate where it no longer conforms to the outline of the observations. To obtain values for calculations we may take the ordinates when the fork is 15 or 20 cm. from the

resonator. In case of nodes farther than 50 cm. from the end of the tube, the observations are taken at such a distance that averages of observations can be taken without the use of the curves.

Effect of Wave-length.—To ascertain the effect of wave-length on correction, three forks were selected; the one generally used having 768 half-vibrations per second, one an octave higher and the third an octave lower. On comparison they were found to differ by an octave to within one tenth vibration per second. Allowing the greatest difference as one tenth vibration an error, in the correction, of .05 cm. could enter into the final result. Curves obtained with these forks are shown in Fig. 4.

Curve.	Fork.	Upper Node.	Correction.	
No. 7	384	47.545	2.052	44.827
No. 6	768	25.035	2.150	22.413
No. 8	1.536	13.945	2.032	11.207

Position of lower node, 69.860 cm. for fork 768.
Top of resonator, 4.770 cm.
Temperature, 23°.55 C.

It will be seen from these observations that the correction for the fork of lowest pitch and for that of highest pitch are nearly alike but the intermediate pitch gives a value a little higher. This may, however, be due to errors in comparison of forks and in observation. Taken together the values point to the conclusion that the correction is independent of wave-length.

Wave-lengths.—Each of the four resonators was provided with four flanges and its own thickness as a fifth flange. The positions of the upper nodes were determined from the curves for each flange (see Figs. 5, 6, 7 and 8). The wave-length was assumed to be twice the distance between the first and second node. Wave-length was determined once for each series of observations which were taken rapidly to avoid changes in humidity. Changes due to temperature were calculated.

Determination of Correction.—From the values of quarter wave-lengths as corrected for temperature, and the positions of the nodes as obtained from the ordinate when the fork may be considered far

from the resonator, the correction can be determined by the use of the formula:

$$x = \lambda/4 - (L_1 - L_2).$$

Wave-lengths as Determined from the First and Second Nodes without a Face-plate on the Resonator.

Resonator.	Upper Node (from Curves).	Lower Node (from Observ.).	Temperature (Observed).	λ
1	23.440	68.290	22.7	22.425
2	24.085	69.090	24.6	22.503
3	25.065	69.950	23.5	22.442
4	24.890	69.650	21.3	22.380

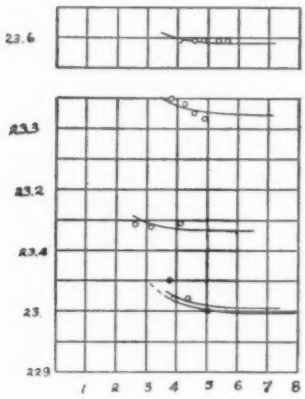

Fig. 5.

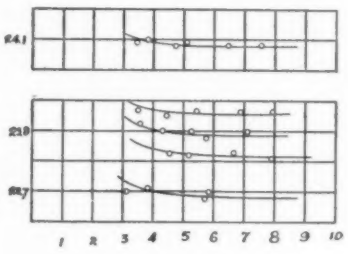

Fig. 6.

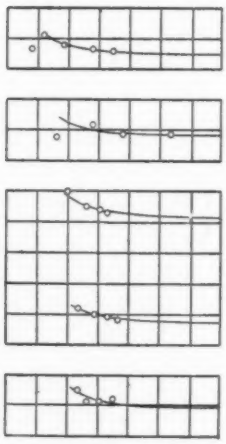

Fig. 7.

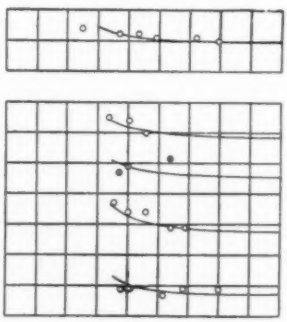

Fig. 8.

x = correction due to open end.

λ = wave-length.

L_1 = position of the upper node.

L_2 = position when the top of the piston is in the same plane as the top of the resonator.

Plotting the relation between width of flange and correction, we obtain the average curve shown in Fig. 9. As may be expected, each curve indicates a tendency to approach a constant value as the width of flange is increased. This enables us to estimate the correction for an infinite flange or, extending the curve in the opposite direction, to determine the correction for a flange of "zero" width. The following table shows a series of the observations.

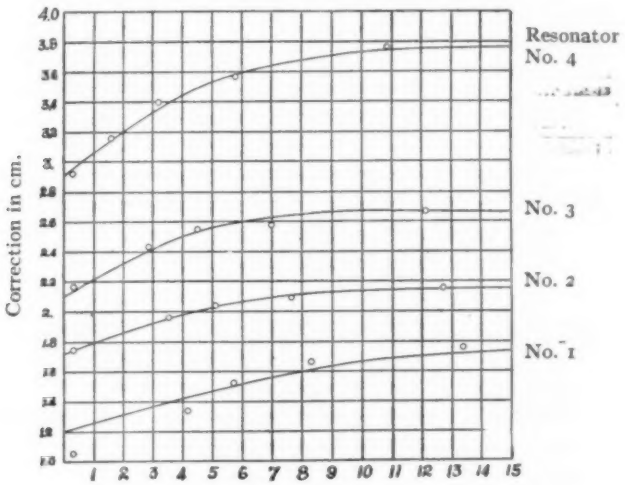

Fig. 9.

Average Correction.—From the above results we see that for a "zero" flange we have the average correction $(.656)R$ which is 15 per cent. above the values obtained by Blaikley. For an infinite width of flange the average is $(.871)R$ which is about 6.5 per cent. above the probable value given by Rayleigh. To test whether these high results were due to the presence of the ceiling which was only 90 cm. above the top of the resonator, the whole apparatus was removed to a

Resonator.	From Curve.			No. 0.			No. 1.			Top at
	Asym.	Temp.	λ/4	Asym.	Temp.	λ/4	Asym.	Temp.	λ/4	
1	23.44	22.7	22.425	23.59	22.7	22.425	23.32	22.9	22.429	
2	24.085	24.6	22.503	24.085	24.6	22.503	23.880	24.75	22.506	
3	25.065	23.5	22.442	25.045	23.5	22.442	24.785	23.55	22.443	
4	24.89	21.3	22.380	24.925	21.3	22.380	24.685	21.3	22.380	
	No. 2.			No. 3.			No. 4.			cm.
1	23.135	22.8	22.427	23.005	22.8	22.427	22.995	22.9	22.429	2.230
2	23.795	24.8	22.507	23.755	24.9	22.509	23.685	24.95	22.510	3.335
3	24.725	23.6	22.444	24.635	23.65	22.445	24.540	23.6	22.444	4.770
4	24.445	21.4	22.382	24.275	21.4	22.382	24.090	21.5	22.384	5.465

	From Curve.		No. 0.		No. 1.		No. 2.		
			Dist. to Top.	Corr.	Dist. to Top.	Corr.	Dist. to Top.	Corr.	
1	21.21	1.215	21.360	1.065	21.090	1.339	20.905	1.522	
2	20.750	1.753	20.750	1.753	20.545	1.961	20.460	2.047	
3	20.295	2.147	20.275	2.167	20.015	2.428	19.955	2.552	
4	19.425	2.955	19.460	2.920	19.220	3.16	18.980	3.402	

			No. 3.		No. 4.		
1			20.775	1.652	20.765	1.664	
2			20.420	2.089	20.350	2.16	Correction in cm.
3			19.865	2.58	19.770	2.674	
4			18.810	3.572	18.625	3.759	

	Inside Radius.	No. 0.	No. 1.	No. 2.	No. 3.	No. 4.	
1	1.903	.328	4.164	5.715	8.305	13.34	
2	2.545	.313	3.483	5.072	7.634	12.697	Width of flange.
3	3.181	.310	2.848	4.437	6.998	12.062	
4	4.447	.310	1.581	3.170	5.732	10.795	

Resonator.	Radius Inside.	"Zero" Flange.		"Infinite" Flange.	
		x	x/R	x	x/R
1	1.903	1.20	.631	3.8	.855
2	2.545	1.73	.680	2.7	.849
3	3.181	2.11	.663	2.19	.861
4	4.447	2.90	.652	1.73	.919

room in which the ceiling was about 600 cm. above the resonator. The results obtained were practically the same except in the case of

resonator no. 1. For this they conformed more nearly to the outline of the curve as drawn in Fig. 9 than observation there shown.

Conclusions.—The length of a resonator responding most to the pitch of a fork depends upon the distance of the fork from the open end.[1] This effect becomes more marked as the resonator becomes shorter and the fork is nearer the open end. A maximum of intensity outside the tube may not indicate that the resonator is nearest to unison with the pitch produced. The correction for a flange of "zero" width is about $(.656)R$ and for a flange of infinite width is about $(.871)R$.

At this point I wish to thank my colleagues, at the Randal Morgan Laboratory, for suggestions and assistance. Especially do I wish to thank Prof. H. C. Richards for suggesting the subject, and Dr. R. H. Hough for suggestions and assistance in obtaining apparatus.

RANDAL MORGAN LABORATORY,
UNIVERSITY OF PENNSYLVANIA,
May, 1910.

[1]R. H. M. Bosanquet, Notes on the Theory of Sound, Phil. Mag., Series 5, Vol. IV., p. 216, 1877.

A PROPOSED METHOD OF CALIBRATION OF OPTICAL PRYOMETERS.

BY G. A. SHOOK.

INTRODUCTION.

FOR the determination of temperatures beyond the limit of the gas scale we must depend, for the present at least, upon the radiation pyrometer which is calibrated in terms of the radiation from a black body. In the case of the optical pyrometers which are in use today, temperature estimation is made by means of a photometric comparison between the red radiation from some standard lamp and the red radiation emitted by the body under observation.

In the Wanner pyrometer the incident radiation is varied by means of a polarizing device, in Le Chatelier by means of an iris diaphragm, and in the Holborn-Kurlbaum or Morse the standard source itself is varied. The last type can only be calibrated empirically by comparison with an experimental black body, but the Wanner or Le Chatelier can be calibrated in terms of Wien's third radiation law and if we assume this law to hold, can be used to estimate temperatures indefinitely high. Wien's law may also be used to extrapolate the empirical calibration of a Holborn instrument so that it can be used for temperatures beyond the limit of the experimental black body, whose range is limited by the platinum thermo-couple.

Wien's law may be written

$$J = C_1 \lambda^{-5} e^{\frac{-C_2}{\lambda T}}, \qquad (1)$$

where J is the energy corresponding to wave-length λ and T is the absolute temperature. C_1 and C_2 are constants and e is the base of the natural system of logarithms.

Equation (1) may also be written in the form

$$\log_{10} J = K_1 - K_2 \frac{1}{T}, \tag{2}$$

where

$$K_2 = C_2 \frac{\log e}{\lambda}.$$

C_2 for a black body equals 14,500 when λ is given in terms of μ.

Equation (2) may be applied to any pyrometer, using monochromatic light, in which the luminous intensity can be varied in a continuous and determinate manner as in the Wanner and Le Chatelier. Either of the instruments will, therefore, indicate temperature indefinitely high, but the limit of accuracy is reached at about 2000° C. so that for higher temperatures the incident radiation is usually cut down by means of one or more absorption glasses. The amount by which it is cut down is determined as follows:

Let J' equal the luminous intensity of the incident radiation and J the value as indicated by the instrument when one glass is used then

$$J' = JR,$$

where R is the absorption factor. For two absorption glasses

$$J' = (JR)R = JR^2,$$

and for n glasses

$$J' = JR^n; \tag{3}$$

also

$$R = J'/J. \tag{4}$$

The general expression then, for the relation between energy and absolute temperature, is from (2)

$$\log J' = K_1 - K_2 \frac{1}{T}.$$

From (3)

$$\log J + n \log R = K_1 - K_2 \frac{1}{T}.$$

Whence

$$t = \frac{K_2}{K_1 - \log J - n \log R} - 273. \tag{5}$$

Where t is temperature in degrees C.

Equation (5) is a general equation for connecting the relation between temperature t and luminous intensity J and can be applied to any pyrometer in which J can be determined theoretically. For the Wanner pyrometer $J = \tan^2 \phi$, where ϕ is the angle of rotation of the nicol analyzer, and for the Le Chatelier $J = (1/d)^2$ where d is the length of one side of the iris diaphragm. K_1, K_2 and R are constants and can all be determined without reference to any temperature observation.

METHOD OF CALIBRATION.

By the usual method of calibrating a Wanner or Le Chatelier pyrometer at least two known temperatures are required, and these are generally obtained by means of an experimental black body. In all subsequent work, therefore, the accuracy of the curve or table, which was constructed for calibration, is subordinate to the accuracy of the observations made on the black body. If this accuracy is increased by observing a large number of points the calibration is complicated by the difficulties inherent in the use of the black body.

It has occurred to the author, in connection with work on radiation pyrometry, that the experimental black body should occupy the same place in optical pyrometry that the gas thermometer does in thermometry, or the Hefner lamp in photometry. While the accuracy of all measurements made in electric light photometry depend, more or less, upon the accuracy with which the secondary electric standard was compared to a primary standard, such as a Hefner lamp, nevertheless it would not be advantageous to always use a Hefner lamp for testing an electric light.

It is the object of this paper to show that the temperature scale of the Wanner, Le Chatelier or any similar optical pyrometer, need not depend upon any temperature observation, one known black body temperature only being necessary to standardize the pyrometer comparison lamp, also that this black body temperature can be obtained by means of a secondary standard, instead of a black body, and that this secondary standard may be used to standardize all pyrometers which must be calibrated empirically, such as the Holborn-Kurlbaum and Morse type.

In order to avoid the use of a black body two different methods have been used with success. The pyrometer to be calibrated and one which has been calibrated can be compared by means of an electrically heated platinum ribbon[1] so mounted that the pyrometers may be directed on opposite sides of the same luminous region. While an observation is being made by the instrument under consideration, the black body temperature of the spot sighted upon can be determined by means of the calibrated pyrometer. In this case both pyrometers must use the same wave-length of light, since platinum departs considerably from black body radiation. In place of the platinum strip a wide filament incandescent electric lamp may be used. This lamp takes less current and can be worked at much higher temperatures. In this case it is not necessary that the pyrometers compared use the same wave-length since an incandescent carbon filament has been shown[2] to be "gray."

Some tests made on the platinum ribbon showed that the temperatures as indicated by a H-K pyrometer, for various values of current through the ribbon, would not repeat themselves after continued burning so no attempt was made to use it as a standard but only to compare pyrometers.

In this case the black body temperature of the region sighted upon can be determined by means of a H-K pyrometer which may be kept as a standard instrument. This, however, is not necessary, since a carefully calibrated pyrometer lamp may always be reserved as a standard of comparison. It has been shown[3] that if such a pyrometer lamp is aged at 1800° C. for about twenty hours it will remain sufficiently permanent for the most accurate work for about fifty hours.

A few preliminary experiments carried out on some of the wide filament lamps showed the possibility of calibrating the same in terms of current and temperature, thus avoiding the use of any pyrometer. The permanence of such lamps has not been thoroughly investigated so that no accurate data can be given. However, from the work of Holborn and Day on other types of incandescent

[1]Bulletin Bureau of Standards, Vol. 1, p. 443.
[2]Bulletin Bureau of Standards, Vol. 2, p. 322.
[3]Bulletin Bureau of Standards, Vol. 1, p. 236.

lamps there is no apparent reason why these lamps should not satisfy the requirements of a secondary black body standard.

It is proposed in the future to obtain some definite data on the ageing of standard pyrometer lamps.

Two methods of calibration will now be developed which are here applied to the Wanner and Le Chatelier although they may be used for any similar instrument.

CALIBRATION OF WANNER PYROMETER.

I. In the case of the Wanner instrument the relation between the ratio of the intensity of the unknown source to the comparison source taken as unity, to the absolute temperature of the unknown source becomes, from (2)

$$\log J = \log \tan^2 \phi = K_1 - K_2 \frac{1}{T}. \tag{6}$$

Equation (6) may be written

$$u = K_1 - K_2 v. \tag{7}$$

Differentiating u with respect to v

$$du/dv = -K_2. \tag{8}$$

This means that the relation between $\log \tan^2 \phi$ and $1/T$ is linear, so that if two temperatures and their corresponding angles of rotation are known, the instrument may be completely calibrated. However, since K_2, the slope of the curve, can be calculated, when the wave-length is known, one temperature is sufficient.

This method has the further advantage that a curve can be drawn for any chosen values of ϕ and T, which will be within limits of the standard lamp, without reference to any temperature whatsoever. A table may be made out with values of ϕ and t for subsequent use. If now the pyrometer be sighted upon any body whose black body temperature is known, the nicol may be set to correspond to this temperature and the current through the incandescent comparison lamp adjusted until a photometric balance is effected. The table made out will then hold for any unknown temperature given therein. The angle for the calibration temperature must be chosen to suit the condition under which the instrument is used, which are in turn

limited by the intensity of the comparison lamp. For instance, if it is desired to have the pyrometer most sensitive at about 1300° C. then the straight line, whose slope is known, should be so drawn that 1300° C. corresponds to 45° (on the nicol analyzer scale) which is obviously the position in which the values of the tangent change less rapidly with a given change in angle. The instrument cannot be used for temperatures much higher than this since the lamp would have to be run at too high a degree of incandescence, which means short life and therefore recalibration. For measuring low temperatures, however, the limit is only reached by the loss of light, which makes a setting very difficult.

This method of calibration will be made clear by an example. For a particular Wanner pyrometer the value of λ was 0.656μ. The slope then from (8) becomes

$$\frac{du}{dv} = K_2 = \frac{c_2 \log e}{\lambda},$$

$$K_2 = \frac{14{,}500 \times 0.4343}{.656}$$

$$= 9{,}600.$$

45° was taken arbitrarily as the reading corresponding to 1000° C.

The following table was then made out.

TABLE I.

t° C.	T° abs.	$1/T$	Rotation, ϕ.	log tan^2 ϕ
1,000	1,273	0.000786	45	0

The curve must pass through the point whose ordinates are 0.000786 and 0 and have a slope of 9,600.

By means of these data curve (5), Fig. 1, was drawn. A Table II. was then constructed with values of ϕ and log tan^2 ϕ. By means of curve (5), $1/T$ was obtained, and finally t was calculated.

Such a table will hold indefinitely for the particular instrument, or in fact for any instrument using the same value of λ.

II. Instead of constructing a table by the above graphical method

TABLE II.

t	T	$1/T$	ϕ	$\log \tan^2 \phi$
788	1,061	0.000942	10	9.493
808	1,081	0.000925	12	9.655
824	1,097	0.000911	14	9.794
1,000	1,273	0.000786	45	0.000
1,242	1,515	0.000660	76	1.206
1,255	1,538	0.000650	78	1.345

a curve coördinating t and ϕ direct may be plotted by means of values calculated from the general equation, (5), which is likewise independent of temperature measurement.

It is seen from (6) that if K_1 were known, various values of ϕ might be substituted in the equation and the corresponding temperatures calculated. Now by assuming some angle of rotation ϕ for some particular temperature T as in the above case K_1 may be found. For example, let

$$T = 1273 \quad \text{and} \quad \phi = 45°.$$

Then from (6)

$$K_1 = \log \tan^2 \phi + K_2 \frac{1}{T}$$

$$= 0 + \frac{9,600}{1,273} = 7.55 .$$

For $\phi = 10$, and $n = 0$, t may be calculated from (5).

$$t = \frac{9,600}{7.55 + 1.51} - 273 \qquad (9)$$

$$= 787° \text{ C.}$$

By substituting various values of ϕ in (9) a series of values of t was calculated (Table III.).

Curve 1, Fig. 2, was plotted from values of t and ϕ. Such a curve will hold indefinitely for any instrument having the same value of λ.

To calibrate the instrument, sight it upon some object whose black body temperature is known. By means of the curve set the nicol analyzer to the angle corresponding to the temperature in question and adjust the standard lamp until a photometric balance is obtained.

TABLE III.

t'	t		$\log \tan^2 \phi - 10$
936	787	10	−1.51
1,040	864	20	−0.88
1,117	922	30	−0.48
1,187	972	40	−0.15
1,256	1,026	50	+0.15
1,341	1,084	60	+0.48
1,457	1,165	70	+0.88
1,679	1,315	80	+1.51

III. A method which requires more observations but somewhat less labor is to calibrate the instrument empirically point by point.

In order to measure temperature beyond the limit of calibration, absorption glasses or mirrors must be used and the absorption factor R must be known. In both methods the temperature may be calculated from (5) and in any event if the apparent temperature, with an absorption glass, is known, the real temperature of the source may be found as follows:

Let J' and T' represent the energy and absolute temperature of the unknown source and J and T the corresponding quantities as determined by the pyrometer when an absorption glass is used. From (4)

$$\log J' = K_1 - K_2 \frac{1}{T'}, \tag{10}$$

and

$$\log J = K_1 - K_2 \frac{1}{T}. \tag{11}$$

Subtracting (11) from (10)

$$\log \frac{J'}{J} = K_2 \left(\frac{1}{T} - \frac{1}{T'} \right).$$

From (5)

$$\log \frac{J'}{J} = R.$$

Therefore

$$\log R = K_2 \left(\frac{1}{T} - \frac{1}{T'} \right),$$

$$\frac{\log R}{K_2} = K = \left(\frac{1}{T} - \frac{1}{T'} \right), \tag{12}$$

whence

$$1/T' = 1/T - K . \qquad (13)$$

Equation (13) is a general equation which may be applied to any pyrometer (based upon Wien's laws) to obtain the true temperature of a body when the incident energy is cut down a known amount by means of either an absorption glass, mirror or a sectored disc, to obtain a photometric balance.

When K is known the calibration of the pyrometer may be extended by the use of one or more absorption glasses whatever method of calibration is used.

For example, in the first method curve *1*, Fig. 1, was constructed so that the instrument could be used for higher temperatures than

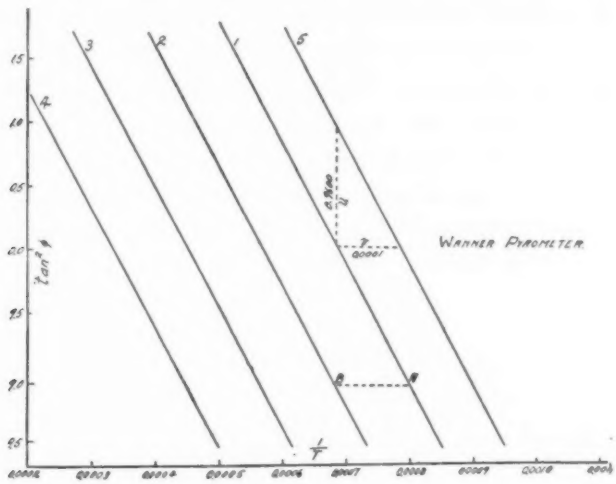

Fig. 1.

are given by curve *5*. In this case 45° corresponds to 1180° C. and curve *2*, which is drawn for one absorption glass, was constructed as follows:

For the absorption glass used, log R was found to be 1.123. From (12)

$$K = \log R/K_2 = 1.123/9{,}600 = 0.000117.$$

Taking any convenient point on curve *1* for $1/T$ as 0.000800, a horizontal distance AB, Fig. 1, equal to 0.000117 was laid off.

A new curve, *2*, parallel to *1* was drawn through the point 0.000683, or what amounts to the same thing

$$1/T' = 1/T - K,$$
$$1/T' = 0.000800 - 0.000117$$
$$= 0.000683.$$

A table was then constructed from this curve as in the above case (Table IV.). Table VI. is similar to IV. only it is used for higher temperatures.

TABLE IV.

No Absorptive Glass.

t	T	$1/T$	ϕ	log tan^2 ϕ
910	1,183	0.000845	10	9.493
938	1,211	0.000826	12	9.655
1,547	1,820	0.000549	78	1.345
1,605	1,878	0.000532	80	1.507

TABLE V.

One Absorptive Glass.

t	T	$1/T$	ϕ	log tan^2 ϕ
1,097	1,370	0.000730	10	9.493
1,127	1,400	0.000714	12	9.655
2,053	2,326	0.000430	78	1.345
2,148	2,421	0.000413	80	1.507

In a similar manner tables can be constructed for two or three glasses. The values of log tan ϕ need be calculated only once and all three values of $1/T$ can be scaled from the three corresponding curves (*2*, *3*, *4*, Fig. 1) at one time.

TABLE VI.

Two Absorptive Glasses.

t	T	$1/T$	ϕ	log tan^2 ϕ
1,358	1,531	0.000613	10	
1,402	1,675	0.000597	12	
2,892	3,165	0.000316	78	
3,105	3,378	0.000296	80	

TABLE VII.

Three Absorptive Glasses.

t	T	$1/T$	ϕ	$\log \tan^2 \phi$
1,743	2,016	0.000496	10	
1,810	2,083	0.000480	12	
4,752	5,025	0.000199	78	
5,314	5,587	0.000179	80	

It will be observed that by means of the above method the pyrometer scale has a range of 788–5314° C.

In the second method a curve for high temperatures may be plotted from values calculated from the general equation (5). For example, curve *2*, Fig. *2*, was constructed the same way as curve *1*,

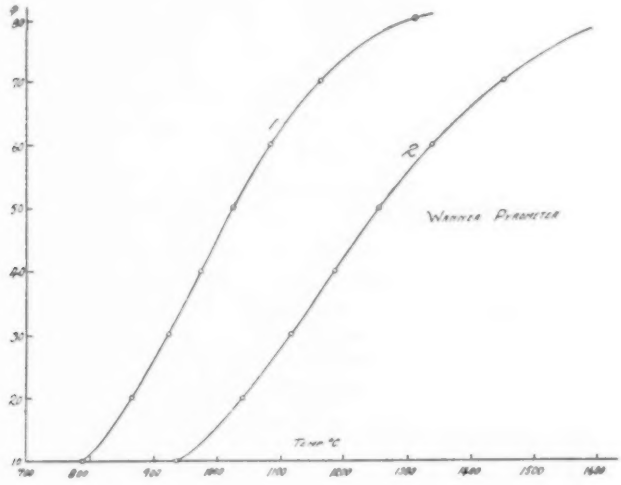

Fig. 2.

except the value of n in equation (5) was 1 and not 0.

$$\text{Log } R = 1.12$$

as in above case. Substituting in (5), for $\phi = 10$,

$$t = \frac{9{,}600}{7.55 - 1.12 - 1.51} - 273$$

$$= 936.$$

A series of values was calculated and tabulated as t', Table III. Curve *2*, Fig. *2*, was plotted with values of t' and ϕ.

If now curve *1* had been determined experimentally, *i. e.*, by point by point comparison as in the third method, curve *2* could be constructed by use of equation (13). A number of values of T may be obtained from curve *1* and the corresponding values of T' calculated for plotting curve *2*. For example, from curve *1* let

$$t = 800° \text{ C.}$$

Therefore $T = 1073$,

$$1/T' = 1/1073 - 0.000117 = 0.000826,$$

$$T' = 1{,}226,$$

$$t' = 953.$$

In a similar manner a table may be constructed, as VIII.

TABLE VIII.

t	T	T'	t'
800	1,073	1,226	953

Since the temperature scale of the Wanner may be constructed when the constants of the instrument are known the idea immediately suggests itself that the scale might be engraved on the divided circle of the analyzer just as we construct scales for photometer bars by means of the inverse square law.

The angle ϕ corresponding to any particular temperature t can be found from the curves in Fig. 1. A drawing of such a scale is shown in Fig. 3. The arms *0*, *1*, *2* and *3* are attached to a tube carrying the nicol analyzer, and move over the graduated scale as shown. For low temperatures, where no glass is used, arm *0* is used in the first quadrant, and for higher temperatures, say between 2000° and 6000° C., arm *3* may be used in the fourth quadrant. The comparison lamp of a Wanner thus equipped may be standardized in a few minutes and then any temperature between 800° C. and 6000° C. may be read directly from the circle.

Such a scale may be used on any Wanner pyrometer using the same wave-length and glasses of same absorbing power.

CALIBRATION OF LE CHATELIER PYROMETER.

Either of the above methods may be applied to a Le Chatelier pyrometer except in this case $J = (1/d)^2$. The gasoline lamp can be adjusted for a photometric balance by raising or lowering the wick.

Equation (5) for this instrument may be written

$$t = \frac{K_2}{K_1 - \log (1/d)^2 \pm n \log R} - 273. \qquad (14)$$

When an absorption glass is placed before the objective n is positive, but when placed before the comparison lamp it is negative.

Fig. 3.

The values of d and t to be used for calibrating must be determined by experiment as the range of the gasoline lamp, burning normally, is rather limited.

Method I. may be applied to this instrument just as it was to the Wanner pyrometer.

The application of method II. will be shown by an example.

The wave-length for the red glass used on a Le Chatelier pyrometer was found to be 0.649μ. The constant K then becomes

$$K_2 = \frac{14{,}500 \times 0.4343}{0.649}$$
$$= 9{,}700.$$

Curves *1*, *2* and *3*, Fig. 4, were plotted from values of d and t calculated from equation (14).

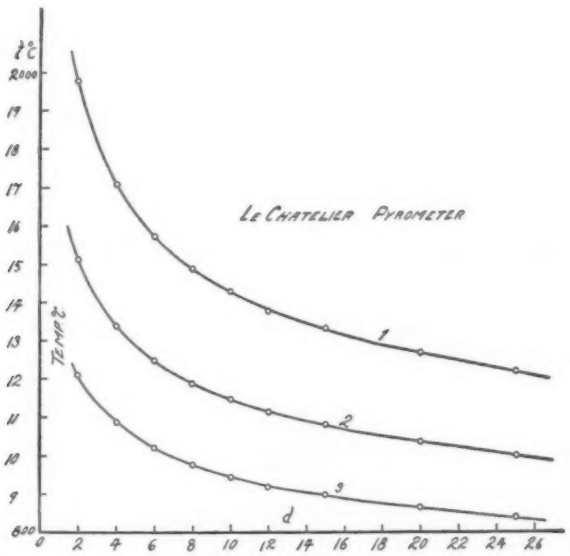

Fig. 4.

Suppose we assume that $d = 25$ when $t = 1000°$ C., then

$$T = 1273,$$

$$K_1 = \log J + K_2 \frac{1}{T}$$

$$= \log (1/d)^2 + K_2 \frac{1}{T},$$

$$K_1 = -2.80 + 9{,}700/1{,}273 = 482.$$

Various values of d were substituted in equation (14) and the cor-

responding values of t calculated, thus for $d = 20$, and $n = 0$,

$$t = \frac{9{,}700}{4.82 - \log (1/20)} - 273 = 1{,}033.$$

For one glass before the objective; $d = 25$, $n = 1$, $\log R = 1.127$,

$$t = \frac{9{,}700}{4.82 + 2.80 - 1.13} - 273 = 1{,}222.$$

For two glasses before the objective; $n = 2$,

$$t = \frac{9{,}700}{4.82 + 2.80 - 2 \times 1.13} - 273 = 1{,}520.$$

For one glass before the comparison lamp (n in this case is negative),

$$t = \frac{9{,}700}{4.82 + 2.80 + 1.13} - 273 = 835.$$

In a similar manner a number of values of t were calculated and Table IX. constructed. The curves in Fig. 4 were plotted from values taken from Table IX. t no glass; t_1 one glass before objective; t_2 one glass before comparison lamp.

TABLE IX.

d	t	t_1	t_2
25	1,000	1,222	835
20	1,033	1,270	861
15	1,080	1,332	895
6	1,247	1,575	1,020
4	1,337	1,712	1,082
2	1,513	1,980	1,210
	Curve 2.	Curve 1.	Curve 3.

CALIBRATION OF HOLBORN–KURLBAUM PYROMETER.

Such an instrument must be calibrated empirically and the calibration will be different for every lamp used. It has been shown,[1] however, that the relation between temperature and current through the lamp may be represented by the general quadratic equation

$$I = a + bt + ct^2,$$

[1]Bulletin, Bureau of Standards, Vol. 1, p. 235.

so that three known temperatures are sufficient to completely calibrate the instrument. Such a pyrometer may be readily calibrated, without the use of a black body, by means of a standard pyrometer comparison lamp as explained above. If such a lamp is not properly calibrated in terms of temperature and current its black body temperature, for any value of current, may be determined by means of another calibrated pyrometer. A platinum ribbon may be used in the same way.

In all experimental work involved in the above no attempt was made for precision, the object being merely to show the possibility of the methods set forth.

PHYSICS LABORATORY,
PURDUE UNIVERSITY.

SOME PHOSPHORESCENT SALTS OF CADMIUM WITH SODIUM.

BY C. W. WAGGONER.

IN an earlier experiment[1] the writer studied the decay of phosphorescence in some simple compounds, among which was a compound of cadmium sulphate and manganese sulphate, made by simply evaporating to dryness a water solution of the two salts. After studying this compound it was placed in a paper envelope and put aside for several months. On taking up work on this substance later it was found that it had lost its power of phosphorescence when excited by the light from the iron spark. On being heated, however, it regained its usual brilliancy; it will be remembered that cadmium sulphate is highly hygroscopic. This led the writer to suspect that the photo-luminescence of these simple salts is only possible when in the anhydrous condition, and subsequent tests showed this to be true for all the compounds studied.

The fact that moisture affects the photo-luminescence of cadmium salts may be shown in a very striking way as follows: Excite the anhydrous phosphorescent compound by an ultra-violet source and then allow the light to decay for several seconds. Now if a drop of water be placed on the decaying compound the residual light will flash out brilliantly for an instant and then disappear very rapidly. It was first thought that this phenomenon was due to the changes which take place within the salt as it takes up water of crystallization. The thermal-phosphorescence of the cadmium compounds is quite marked, and Dr. Kortright, of the department of chemistry, West Virginia University, suggested to the writer that the effect might be partly due to thermal-phosphorescence brought about by the rise in temperature which accompanies the process of hydration. To obtain some idea of the amount of rise in temperature, several grams of anhydrous salt were placed in a test-tube, and the tempera-

[1] PHYS. REV., Vol. XXVII., p. 209, 1908.

ture rise measured by a mercury thermometer when water was added. This was found to be as much as 5° C., the amount of water being small. This rise of temperature would account in a large measure for the phenomenon purely on the basis of thermal-phosphorescence. Alcohol, which is not a solvent for cadmium sulphate, was tried, but gave no effect.

The fact these cadmium compounds do not show photo-luminescence when in the crystalline state led the writer to try some of the original cadmium sulphate from which the compounds with manganese were made; and when the water of crystallization was driven off, the salt was found to be highly phosphorescent when excited by an ultra-violet source, the color of the phosphorescence being similar to that when a manganese salt had been added, but not having the same intensity. When subjected to kathode rays the sulphate showed more brilliant fluorescence but less phosphorescence than when excited by the spark.

An attempt was first made to purify the original cadmium sulphate by forcing it out of water solution with sulphuric acid, but this treatment increased rather than decreased the intensity of phosphorescence.

Another method was to precipitate the cadmium with hydrogen sulphide as cadmium sulphide, wash it with water till free from sulphates, then redissolve the sulphide in sulphuric acid, crystallizing the salt formed. This sulphate still gave a brilliant yellow phosphorescence under both the iron spark and the kathode rays.

The next method was to crystallize the salts in fractions from water which was slightly acidified with sulphuric acid to prevent hydrolysis. The mother liquor was saved in this case and the crystals redissolved and crystallized out. It was found that the phosphorescence of the successive crystals, as they separated out from the retained mother liquor, decreased rapidly in intensity and at the end of the seventh fractionalization was almost nil, thus indicating the presence of an impurity less soluble than the cadmium sulphate; this view was supported by a micro-chemical test made by Dr. Wilkinson,[1] showing the presence of sodium and a slight trace of zinc.

In casting about for a cadmium sulphate free from this phos-

[1]Journal of Physical Chemistry, Vol. XIII., p. 719, 1909.

phorescence, samples of a number of manufactures were tried and it was found that the "tested purity" cadmium sulphate made by Eimer and Amend was free from this phosphorescence to a remarkable degree. The phosphorescence, under the iron spark, of the anhydrous powder was so small that it was necessary to stay in the dark room quite a long time before the eye became sensitive enough to detect the phosphorescence at all; and even then, one could not be sure of the color. The analysis of this material given on the bottle, was as follows: "CdO, 52.84 per cent.; SO_3, 47.15 per cent.; As, none; Zn, none." This material was tested by the kathode rays and it was found to show neither fluorescence nor phosphorescence. Having found a phosphorescent-free cadmium sulphate it was decided to try to reproduce the phosphorescence by the addition of sodium and zinc salts. The compounds made with cadmium by the addition of various sodium salts were taken for the major work on this paper.

That a zinc salt, when added to a cadmium salt, or vice versa, would produce a phosphorescent compound had been pointed out by Wiedemann and Schmidt.[1] This fact led to the suggestion that the presence of small traces of zinc in cadmium salt, or vice versa, might be detected by the photo-phosphorescence which these compounds show, and some rough tests were made showing photo-phosphorescence with less than one part of zinc sulphate in 10,000 parts of the phosphorescent-free cadmium sulphate. The phosphorescent color was green, but the intensity was not as great as when a sodium salt is added to a cadmium salt.

The pure cadmium sulphate is very susceptible to a small impurity; how susceptible will be shown by the following experiment which was tried. Some water, which had been twice distilled in an all-glass still, was placed in a bottle and allowed to stand over night; the following day this water was used to dissolve some of the pure cadmium sulphate and was then driven off. When the cadmium sulphate was tried under the ultra-violet source it was found to be highly phosphorescent. Two hundred cubic centimeters of this same water when evaporated down in a platinum dish left a residue so small that it could not be seen except when the platinum dish was at red heat.

[1] Wied. Ann., Vol. 56, 1895.

The method of preparing the compounds of cadmium with sodium was that used in a previous paper[1] and was suggested by the work of Wiedemann and Schmidt.[2] It was to dissolve the crystals of sodium salt and cadmium sulphate in water; slowly evaporate the solution to dryness and test the compound for phosphorescence when it had reached the temperature of the room, by exciting by the iron spark. The compound, from the original crystals to the final test, was kept in a large platinum dish and it is needless to say that every precaution was taken to prevent impurities from entering the solution.

The water was twice distilled in an all-glass still and used immediately in order to prevent it from taking up sodium from the glass container. To produce an even and easily regulated temperature a small electric furnace was made by wrapping "Nichrome" ribbon around a porous battery cup; this proved to be a very satisfactory arrangement, for the platinum vessel could be placed on the inside of this furnace and covered over lightly to prevent impurities from the air entering while evaporation was taking place.

Only readily soluble salts of sodium were used; and each one was tested in the anhydrous condition for the presence of phosphorescence. In one or two cases it was necessary to recrystallize the salt to free it from the impurity causing the phosphorescence. A number of different percentages of cadmium and sodium were tried and it was found that the phosphorescent intensity depends somewhat upon the percentage of the sodium present, but so far as the tests were carried no change was produced in the phosphorescent color by rather wide variations in the percentages of the added sodium. In most cases of the compounds recorded in Table I. the amount of sodium salt present was not far from one per cent.

An inspection of Table I. shows that the color of the phosphorescence of cadmium salts with sodium ranges from blue to yellow. In all but two cases the intensity was very small; so small as to make it impossible to obtain reliable curves of decay from these compounds with a spectrophotometer.

Doubtless all of these could be increased in intensity by finding

[1] *Loc. cit.*
[2] *Loc. cit.*

Sodium Salt Added.	Phosphorescent Color.	Spectrum.
Na_2SO_4	Yellow.	
$Na_2S_2O_3$	No phosphorescence.	
Na_2SiO_3	Blue.	.486μ, max...510μ, .604μ.
Na_4HPO_4	Faint green.	
$NaNO_3$	Faint yellow.	
Na_2MnO_4	Greenish yellow.	.522μ, max...566μ, .616μ.
NaFl	Greenish yellow.	.474μ, max...574μ, .612μ.
Na_2CrO_4	No phosphorescence.	
NaOH	No phosphorescence.	
NaCl	Green.	.510μ, max...——, .580μ.
$NaClO_3$	Faint yellow.	
Na_2CO_3	No phosphorescence.	
NaBr	Blue.	.414μ, max... 480μ, .600μ.
$Na_2B_4O_7$	Pale green.	
$Na_2Cr_2O_7$	No phosphorescence.	
$Na_2SO_4Al_2(SO_4)_3$	Faint green.	

the suitable proportion of sodium to add to bring about the highest intensity. However several had sufficient intensity to permit of a study of the decay.

A NEW PHOSPHOROSCOPE.

It was found that the time of decay in the cadmium compounds was much longer than the decay of the compounds studied in a former paper, and that the phosphoroscope there described[1] was not suited to the study of the cadmium-sodium compounds. A new phosphoroscope was built, retaining the main features of the first machine as far as possible and yet increasing the limit of time through which the decay might be studied. This machine is a modification of a phosphoroscope used by Kester[2] in studying the decay of calcium sulphide; the essential difference lies in the fact that with this machine it is possible to study the decay without changing the time of excitation. This feature is one of considerable importance in the design of a phosphoroscope since without it another variable, namely, variable excitation, affects the form of the time-intensity curves. That the original Becquerel phosphoroscope was not free from this objection has been pointed out by Nichols and Merritt.[3]

Fig. 1 shows the top view of the apparatus for making the decay

[1] *Loc. cit.*, p. 202.

[2] PHYS. REV., Vol. IX., p. 164, 1899.

[3] PHYS. REV., Vol. XXII., p. 280, 1906.

curves. *W* is an iron pulley 18 inches in diameter mounted on a vertical shaft. The pulley when mounted was found to run very true and its mass acted as a balance wheel on the driving motor to keep the speed constant. The speed was automatically recorded on a chronograph. The compound to be studied was sifted lightly over a strip of paper covered with "Zapon" varnish; the strip of paper was then placed on the rim of the pulley. The spark gap *S* was mounted in such a way that it could be moved to different points on the periphery of the wheel without in the least disturbing the speed of the wheel or the continuity of the spark. This made

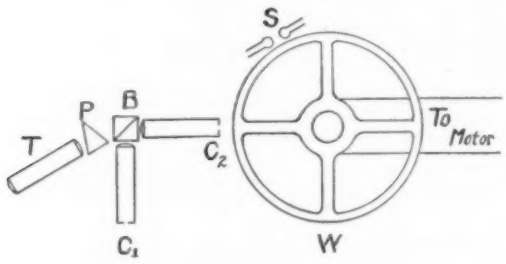

Fig. 1.

Showing the top view of the phosphoroscope.

it possible to maintain a constant excitation and still obtain the intensity of the phosphorescence at various times after excitation. The phosphorescent light to be studied enters the Lummer-Brodhun spectrophotometer at C_2, the comparison source is shown at C_1, the telescope at *T*. One very serious difficulty was encountered in the method above. It was found impossible to get an even layer of the phosphorescent material on the paper strip, especially of such a length ($3\frac{1}{2}$ feet); however, in operation the spectrophotometer showed no perceptible variation in the intensity due to inequalities on the surface even at very slow speeds; and since several seconds or longer were necessary to make a reading, the curves give an average effect. Again, the "Zapon" varnish is not an ideal binder for the phosphorescent material, for as the varnish hardens it becomes brittle, allowing the material to drop from the strip.

Fig. 2 shows the phosphorescent spectrum of a cadmium-sodium-

manganate taken with a spectrophotometer using an incandescent lamp as the comparison source.

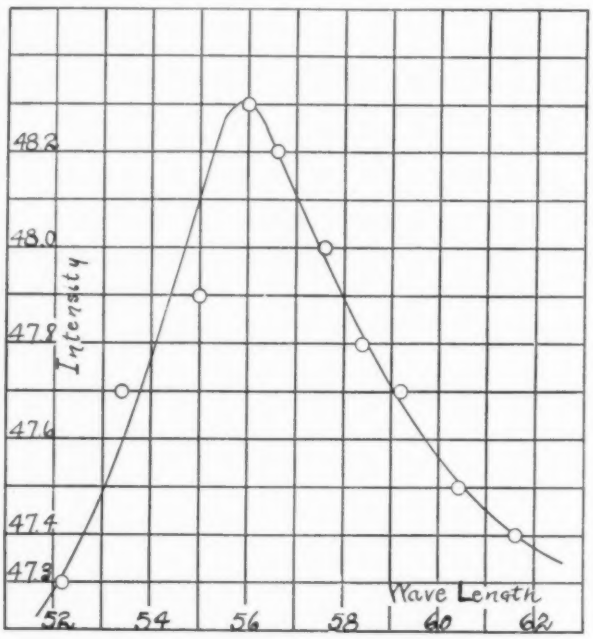

Fig. 2.

Showing the phosphorescent spectrum of a Cd-Na_2MnO_4 compound, taken .374 second after excitation.

Fig. 3 shows the phosphorescent spectrum of a cadmium-manganese-chloride compound. An inspection of these two curves shows that the energy distribution is very similar. In earlier experiments it was found that the phosphorescent spectrum of a cadmium-manganese-sulphate compound extended from .514 to .623 with a maximum at .565. It would seem from these results that the manganese salts produce, when added to a cadmium salt, a phosphorescent compound whose spectrum shows the same maximum, and is independent of the salt.

Of the sodium salts this is not true, for the colors are widely different. An attempt was made to measure the spectrum of all the sodium compounds, but in most cases the intensity was far too small to measure.

Decay curves were taken from all the compounds whose intensity was sufficient to measure. All these curves show the same char-

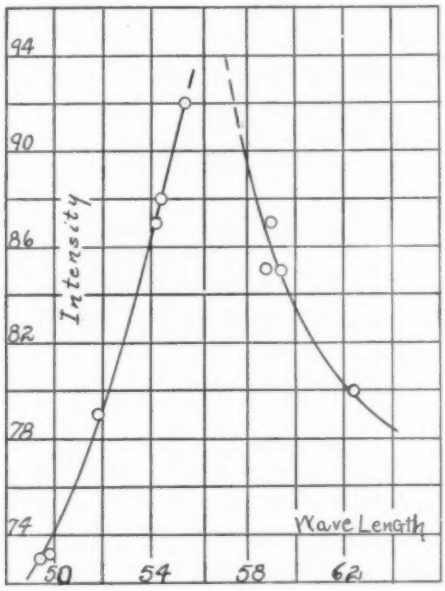

Fig. 3.

Showing the phosphorescent spectrum of a $CdSO_4$-$MnCl_2$ compound, taken 1.44 seconds after excitation.

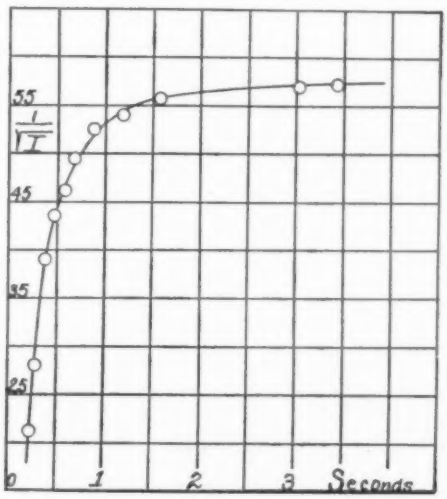

Fig. 4.

Showing the curve of decay of a $CdSO_4$-NaBr compound.

acteristics when plotted with the reciprocal of the square root of the intensity as ordinates and time in seconds as abscissas. Fig. 4 gives the decay curve for a cadmium sulphate with sodium bromide, and exhibits the two straight lines merging into each other.

The work above described was done in the physical laboratory of Cornell University, and the writer wishes to thank Professors Nichols and Merritt for their many suggestions while the work was go ng on.

WEST VIRGINIA UNIVERSITY,
April, 1910.

A STUDY OF THE SHORT-TIME PHOSPHORESCENCE OF CERTAIN COMPOUNDS.

By Carl A. Zeller.

THE following article treats of the decay of phosphorescence of four groups of compounds, namely, the aniline dyes in their solid form; a group of manganese compounds of known percentage concentration, and a group of cadmium compounds, both prepared by C. W. Waggoner; and a group of four phosphorescent sulphides furnished by Leppin and Masche, and prepared by the method of Lenard and Klatt.

It was thought that the aniline dyes which show fluorescence in solution might show phosphorescence when in the solid form. The manganese group would give the relation between intensity and percentage concentration. The cadmium group prepared by Waggoner had not yet been studied at all. The special reason for studying the sulphides was to determine whether the decay curves showed any deviation from the usual form during the first few hundredths of a second after the end of excitation. The only decay curves that have been determined for compounds of this type during this early stage of decay are apparently those published by Waggoner for Sidot blende.[1]

The phosphoroscope[2] and photometer used are shown in Fig. 1. The disk D is fastened to the horizontal shaft N. Inside of this hollow shaft N is a shaft R, which extends back to the hollow shaft F, and is connected to F by a pin, which, working in a spiral groove, allows R to be rotated, relative to N, by sliding the rod K back and forth. The mirror M is set on the end of shaft R, at an angle of 45° to its axis. The shaft F is connected to N, so that R, N and F all rotate together, at the same speed. The arrangement allows the mirror M to be turned through any angle, relative to

[1] Phys. Rev., Vol. XXVII., No. 3, p. 209, 1908.

[2] The phosphoroscope was the same that was used by Waggoner (l. c.).

the disk, while the disk is spinning. The shaft N is driven by a motor belted to the pulley E. The spiral thread P drives the wheel H, which makes electrical contact every hundred revolutions, giving a means of recording the speed. The opening in the disk at O allows the light from the iron spark, S, to fall on the specimen once every revolution. The time of excitation depends on the speed of the disk and the size of the opening, which can be regulated.

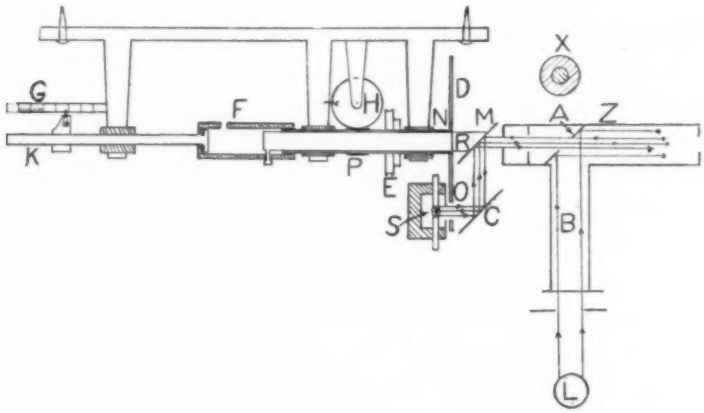

Fig. 1.

The mirror M reflects the light from the specimen into the photometer, and through the hole in the mirror A to the eye. By the rod K the mirror M can be turned so as to reflect the light into the photometer after excitation. For example, running the disk at 600 R.P.M. with an opening of 90°, gives an excitation of .025 sec. and cuts off the exciting light for .075 sec. The machine at this speed allows the phosphorescence to be studied for .061 sec. before another period of excitation. The scale G gives a means of determining the number of degrees through which the mirror has been turned. This apparatus allows the time of excitation to be kept constant, and any number of readings may be made for the same point on the curve. The Wehnelt interrupter was adjusted until the high tone of the spark indicated a high frequency. The spark was enclosed in a wooden block to deaden the sound and concentrate the light. The whole apparatus was painted black, and the specimen C, mirror M, and the end of the photometer Z, were so enclosed as to eliminate all stray light.

The photometer Z was made of two brass tubes set at right angles, with a mirror A, set at 45°, at the point of intersection of their axes. The mirror was made by grinding a piece of microscopic slide glass into the form of an oval, and cutting a hole in the center. The glass was then silvered. This gave a comparison field x, with the phosphorescent light in the center. The color match was obtained by using color slides made from aniline dyes, dissolved and flowed on glass. By using single colors or combinations an exact match was obtained. Inside reflection was shut off by painting the inside of the tubes dead black, and by the use of diaphragms.

The Aniline Dyes.

The aniline dyes were dissolved in either zapon, gelatin, water glass, or collodion, and flowed on glass. The glass proved to be too phosphorescent for its use; even oxidized brass emitted some light. Finally black broadcloth was used as a back-ground, and the samples tested in powdered form, the phosphoroscope running at 2200 R.P.M. From a lot of fifty samples obtained from Heller and Merz, of New York, the following show both fluorescence and phosphorescence in slight degree: Naphthyl carmine, white; *F* blue, *P* very slight; naphthyl sodium disulphonate, gray; *F* blue, *P* slight; phthalic anhydride, white; *F* light blue, *P* slight; naphol sodium disulphonate, gray; *F* blue, *P* slight; naphol sodium monsulphonate, gray; *F* blue, *P* slight; naphol sodium sulphonate, gray; *F* blue, *P* trace; beta-naphthol, white; *F* light blue, *P* trace; tetrachlor phthalic anhydride, white; *F* blue, *P* slight; alpha naphthylamine; *F* violet, *P* slight; nitro-naphthylamine, light yellow; *F* green, *P* slight; sulphonate of soda, reddish; *F* blue, *P* slight. Several of these show marked fluorescence when dissolved. Eosin, fluorescein, and rhodamin, in powdered form, show no trace of phosphorescence.

The Manganese Chloride Group.

The samples were placed on brown cardboard with Zapon varnish. The phosphoroscope ran at 600 revolutions per minute, or one revolution per 0.1 sec. Time of excitation .025 sec. The limit of the machine at this speed is .061 second. The zero point on the

scale was determined by readings taken at the point where reflected white light just disappeared. In making a reading the mirror was turned just far enough to shut off the direct reflected light. The standard was then moved until a definite match was obtained. The rest of the readings were made by moving the standard lamp one division and turning the mirror away from the zero point. The dimness of the phosphorescent light and the limit of the machine allowed but seven or eight points at most. The data plotted are the averages of three or four readings. The color for this group is a pinkish red. In Fig. 2, the curves are plotted with time of decay

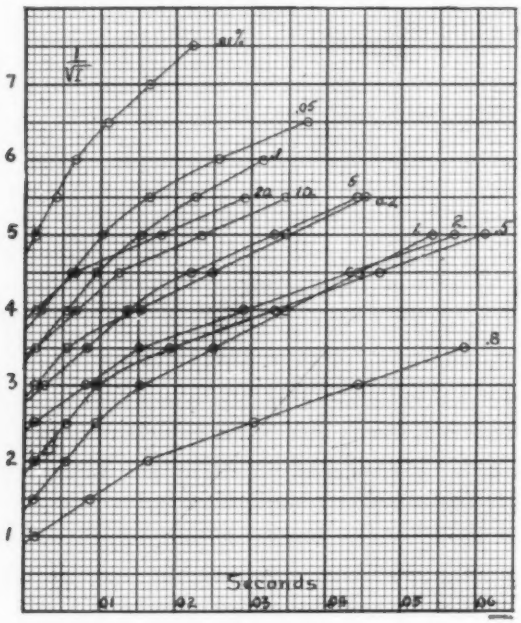

Fig. 2.

Manganese chloride group, ranging from .01 per cent. to 20 per cent. concentration. Ordinates proportional to the reciprocal square root of the intensity of phosphorescence.

as abscissæ and $1/\sqrt{I}$ as ordinates, $1/\sqrt{I}$ being proportional to the distance of the standard lamp from the photometer screen. The lower and upper parts of the curves are straight lines, becoming concave downward as they approach each other. Several of the curves happen to have points taken at the bend and would indicate

two straight lines meeting. All of the curves plotted with I^{-1} as abscissæ show the upper and lower parts as straight lines, gradually merging into one another.

The curves are in fact of exactly the same type as the decay curves obtained by Nichols and Merritt with Sidot blende.[1] A glance at the curves in Fig. 2 show a marked tendency toward parallelism in both parts. According to the assumption of Wiedemann and Schmidt, that the light is emitted during the recombination of the products of the dissociation produced during excitation,

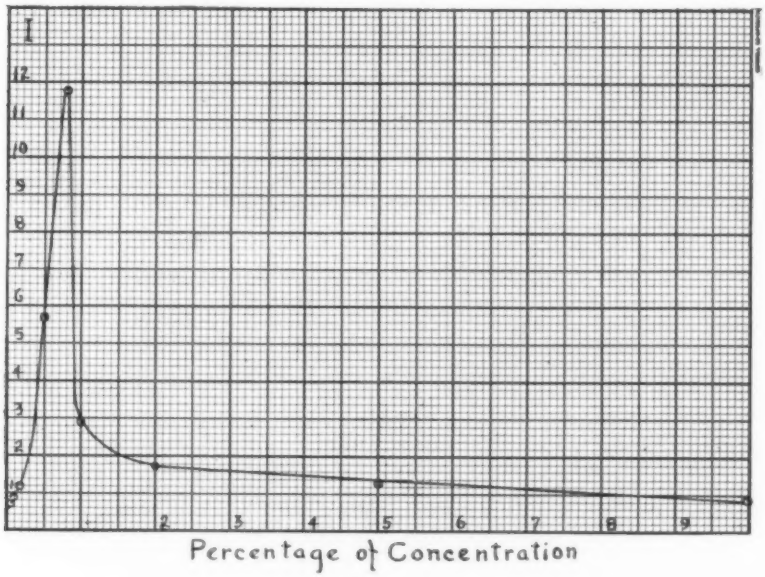

Fig. 3.

Showing the relation between intensity and percentage concentration.

this would indicate the same coefficient of recombination of the ions for the lower parts of these curves, and the same though a slower recombination in the upper parts. In this group the compounds that have the greatest initial intensity have the longest period of decay, although there seems to be no relation between the initial intensity and the time of decay. The cadmium compounds show just the opposite relation. The different slant in the

[1] PHYS. REV., Vol. XXIII., No. 1, July, p. 39.

two parts of the curves indicates a different coefficient of recombination and a different rate of decay for the two parts. The coefficient and the decay are smaller in the second part, showing a much slower process in the giving back of the stored energy.

The greatest intensity was shown by the compound of .8 per cent. concentration. The relation between percentage concentration and

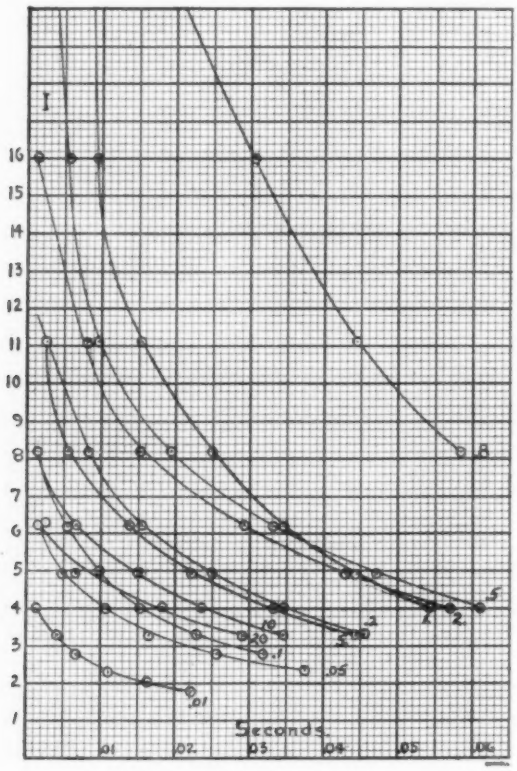

Fig. 4.

Manganese chloride group. The ordinates are proportional to the intensity of phosphorescence.

initial intensity is shown in Fig. 3 by plotting percentage concentration as abscissæ and initial intensity as ordinates. The initial intensities were obtained by extending the straight line of the first part of the curves in Fig. 2 to the y axis and reading the y intercept from the scale.

In Fig. 4 the curves are plotted with time as abscissæ and intensity as ordinates. These curves show the real decay, but do not bring out the first and second process.

The Cadmium Group.

The phosphorescence of the cadmium compounds is yellow green. Fig. 5 shows the decay curves for three different compounds. These are characteristic decay curves, and follow the general form. The

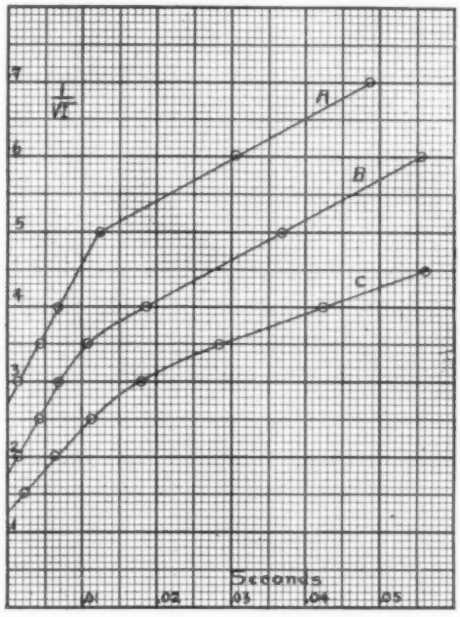

Fig. 5.

Decay curves for three cadmium compounds. The color of phosphorescence is green in each case. Time of excitation = .025 sec.

A, $CdSO_4 + MnSO_4$; *B*, $CdSO_4 + MnCl$; *C*, $CdSO_4 + MnCl$—different percentage.

compounds $CdSO_4 + NaCO_3$, $CdSO_4 + NaClO_3$, $CdSO_4 + NaCl$, $CdSO_4 + NaNO_3$ and $CdSO_4 + NaBr$, were too dim to measure but when excited, may be seen in a dark room for several minutes. In this group the specimens that have the most intense phosphorescence have the most rapid decay.

LONG-TIME DECAY SUBSTANCES.

A number of phosphorescent sulphides, made by the Lenard and Klatt method,[1] were obtained from Leppin and Masche, Berlin. They consist of a sulphide, an active metal, and a flux. Practically all long- and short-time decay curves have shown two distinct processes, merging into one. By this method it was possible, using

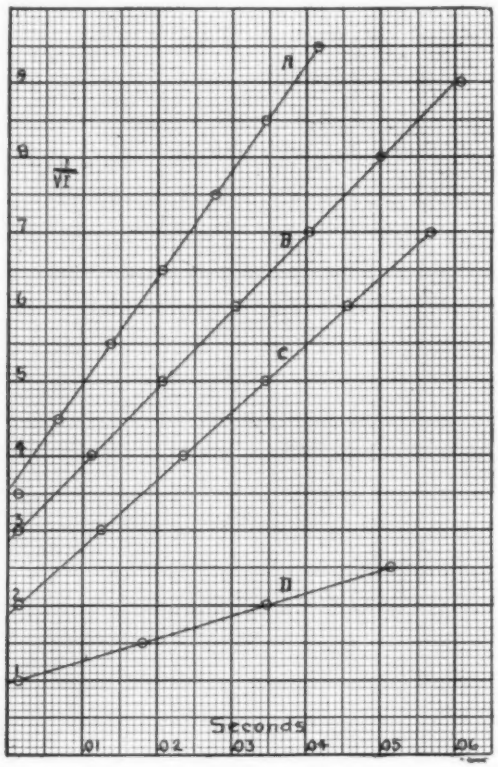

Fig. 6.

A, Sr-Bi-Na phosphorescence, green; *B*, Sr-Zn-F phosphorescence, green; *C*, Ca-Bi-Na phosphorescence, violet; *D*, Ba-Cu-Li phosphorescence, orange-red.

long-time specimens, to study the first part of the first process, for the very first interval of decay. The specimens were excited for .008 sec. and the first readings made .0014 sec. after excitation. The curves shown in Fig. 6, plotted with time as abscissæ and $I^{-\frac{1}{4}}$

[1] Kayser, Handbuch der Spectroscopie, Vol. 4, p. 750.

as ordinates, are in all cases straight throughout the range studied. These results, which are in agreement with the results of Waggoner for Sidot blende, make it appear quite improbable that the behavior of the phosphorescent sulphides during the early stages of decay can be represented by an exponential law, as has sometimes been assumed.[1]

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[1]Werner, Annalen der Physik, Vol. 24, p. 164, 1907. Lenard, Annalen der Physik, Vol. 31, p. 641, 1910.

STUDIES IN LUMINESCENCE.

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

XII. THE ABSORPTION OF ALCOHOLIC SOLUTIONS OF EOSIN AND RESORUFIN.

IN the case of the fluorescent solutions there is every reason to believe that the fluorescence is a property of the ion. It is a matter of interest therefore to determine whether the absorption of these solutions is also an ionic property or whether the absorption may be due in part at least to the undissociated substance. Some light may be thrown upon this question by studying the absorption in dilute and concentrated solutions. If the absorption is partly due to the undissociated molecules and partly to the ions we should expect some change in the form of the absorption curve to result from change in concentration, since in dilute solutions the undissociated molecules will form a smaller proportion of the whole.

For these reasons, and because of the fact that certain experimental work with eosin and resorufin made it desirable to know the absorbing power with considerable accuracy, we have determined the coefficient of absorption for different wave-lengths throughout the absorption band for both dilute and relatively concentrated solutions of these two substances.

The method used consisted in comparing the intensity of the light transmitted by a cell containing pure alcohol with the transmission, for the same wave-length, when the cell was filled with the solution in question. For the concentrated solutions two cells were used, whose thickness was 1 cm. and 3 cm. respectively. The dilute solutions were contained in a cell whose length was 29.5 cm. The source of light for transmission was an acetylene flame. The comparison standard was also an acetylene flame, which was mounted so as to slide upon a track, as described in our last paper.

The ratio of the intensity of the light transmitted by the solution to the intensity of the light transmitted by the alcohol gave the

percentage transmission, from which, with the thickness of the cell, the coefficient of absorption, α, could be computed, α being defined by the expression

$$I = I_0 e^{-\alpha x}$$

where x is the thickness.

The results for eosin are shown in Fig. 88 and for resorufin in

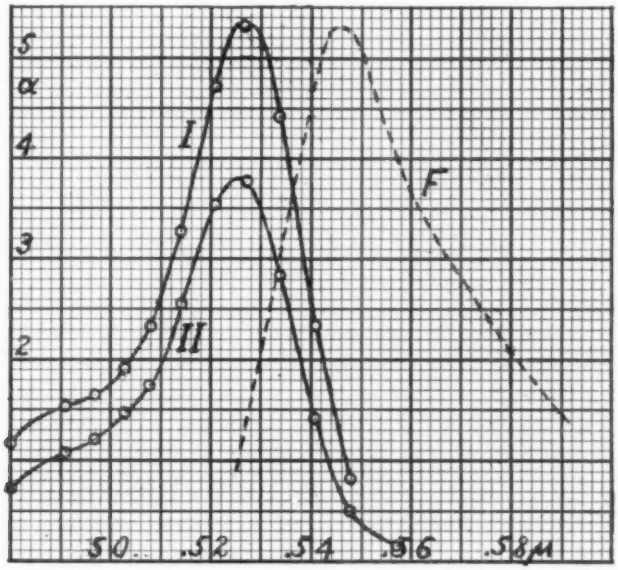


Fig. 88.

Eosin. Curve *I* shows the coefficient of absorption as a function of the wave-length for a dilute solution Curve *II* shows the same thing in the case of a concentrated solution. (The vertical scale in curve *I* is fifty times greater than that of curve *II*.) Curve *F* shows the distribution of energy in the fluorescence spectrum of fluorescein.

Fig. 89. Curve *I* in each case gives the coefficient of absorption for the dilute solution as a function of the wave-length, while curve *II* gives the coefficient of absorption for the concentrated solution. In Fig. 88 the scale is fifty times greater for curve *I* than for curve *II*, and in Fig. 89 the scale for curve *I* is ten times as large as that for curve *II*.

It will be seen that the absorption curve has very nearly the same form for the dilute and concentrated solutions. This is especially

true in the case of resorufin, where each little ripple on the curve for the dilute solution is reproduced on the curve for the concentrated solution. In Table I. will be found the values of α for the

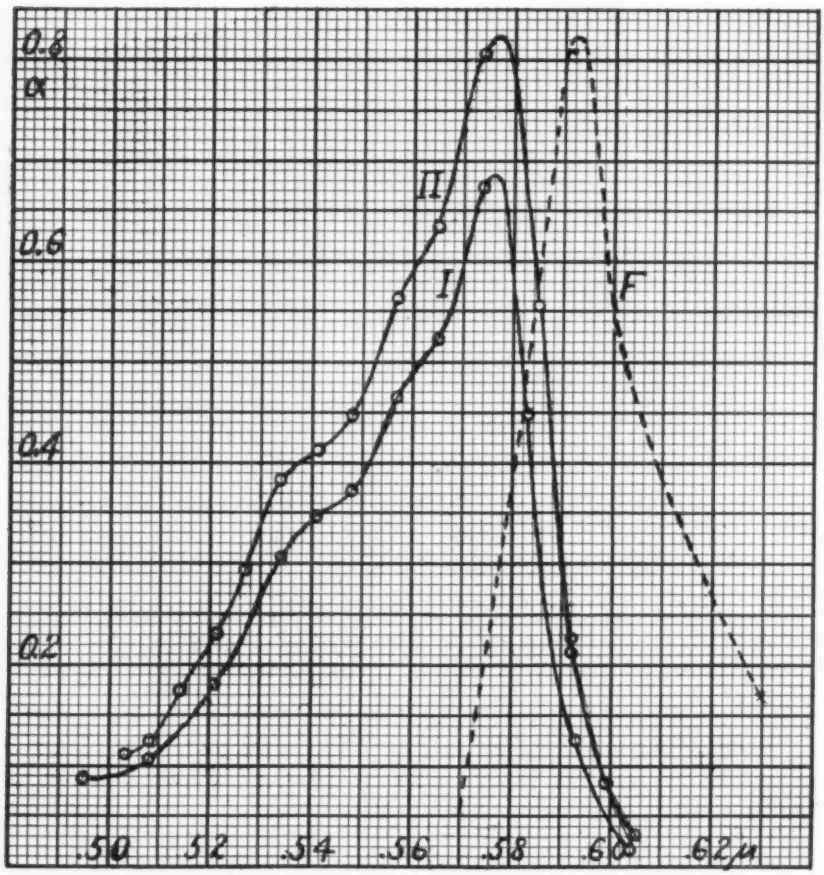


Fig. 89.

Resorufin. Curve *I*, coefficient of absorption for dilute solution; Curve *II*, coefficient of absorption for concentrated solution. (The scale of Curve *I* is ten times greater than that of Curve *II*.) Curve *F* shows the energy distribution in the fluorescence spectrum.

two solutions together with the ratio of the two values. It will be seen that the ratio remains nearly constant throughout the whole spectrum. The variation from constancy is most marked at the

TABLE I.

Coefficients of Absorption for Resorufin.

λ	a_1 Dilute.	a_2 Concentrated.	Ratio, $a_2 : a_1$.
.497μ	.0078		
.503		0.112	
.508	.0107	0.125	11.7
.514		0.175	
.521	.0180	0.232	12.9
.527		0.299	
.534	0.0307	0.385	12.6
.541	0.0349	0.414	11.8
.548	0.0372	0.448	12.0
.557	0.0467	0.563	12.0
.565	0.0522	0.637	12.2
.574	0.0674	0.807	12.0
.583	0.0448	0.576	12.8
.585		0.557	
.593	0.0126	0.162	12.9
.599		0.084	
.604	0.0017		
.605		0.032	

two ends of the spectrum, where the liability to experimental error is greatest. The results in the case of resorufin appear to indicate that the form of the absorption curve is not altered by concentration throughout the range studied, and are thus in agreement with the results of Miss Wick.[1]

TABLE II.

Coefficients of Absorption of Eosin.

λ	a_1 Dilute.	a_2 Concentrated.	Ratio, $a_2 : a_1$.
.480μ	0.0116	0.356	30.7
.491	0.0153	0.540	35.3
.497	0.0166	0.597	35.9
.503	0.0192	0.736	38.3
.508	0.0233	0.870	37.2
.514	0.0328	1.274	38.7
.521	0.0473	1.765	37.3
.527	0.0533	1.892	35.6
.535	0.0444	1.422	32.0
.541	0.0235	.715	30.3
.548	0.0083	.250	30.1

[1] PHYS. REV., Vol. XXIV., p. 356, 1907.

The appearance of the curve for resorufin suggests that the band is complex and that in addition to the principal maximum at .577μ there are secondary maxima of absorption at about .558μ and .536μ. If the absorption of resorufin really consists of three overlapping bands, as seems probable, our results indicate that all three of these bands are produced by the ions.

In the case of eosin there is some indication of a secondary maximum in the neighborhood of .49μ. The values of α for the two solutions and the ratios for these two values are given in Table II. It will be noticed that the ratio is not so nearly so constant as in the case of resorufin. There is perhaps some slight indication that the secondary band at .49μ changes with the concentration at a different rate from the principal band; but it is doubtful whether the results are sufficiently accurate to give any certainty to such a conclusion. The small values of the ratio on the red side of the band imply a slight shift toward the red in the case of the dilute solution; but the region in which these small values in the ratio occur is the region where the results are most liable to error.

In each case we have shown by the curve F the distribution of energy in the fluorescence spectrum of the substance in question. The resemblance between this curve of energy distribution and the absorption curve is quite noticeable. Roughly speaking the one curve is the image of the other. In the absorption curve the side toward the red is steep while the absorption dies away gradually toward the violet. In the fluorescence curve the intensity dies away gradually towards the red and stops abruptly on the violet side. When the mechanism of fluorescence is more fully understood the reason for this peculiar relationship between the two curves, which seems to be a characteristic of the fluorescent substances of this class, will doubtless be clear.

STUDIES IN LUMINESCENCE.

By Edward L. Nichols and Ernest Merritt.

XIII. The Specific Exciting Power of the Different Wave-Lengths of the Visible Spectrum in the Case of the Fluorescence of Eosin and Resorufin.

In the case of either a solid, like anthracene, or of a liquid such as one of the fluorescent dyes, fluorescence may usually be excited by light of a great variety of different wave-lengths. In fluorescent solutions there is usually a well-marked absorption band lying close to the fluorescence band on the side toward the violet, and light of any wave-length within the limits of this absorption band will excite fluorescence. In fact fluorescence may usually be excited by light of much shorter wave-length, so that the solution will be lighted up when exposed to an ultraviolet spectrum. Simple inspection, however, is sufficient to show that the intensity of the fluorescence excited by different portions of a given exciting spectrum is widely different. It is not clear whether this variation is due to the fact that certain wave-lengths are particularly effective in exciting fluorescence, or whether it results merely from the fact that the absorbing power of the material is different for different wave-lengths. It is clear that light cannot produce excitation unless it is absorbed by the fluorescent solution. Differences in absorbing power might therefore produce wide variations in the apparent effectiveness of different spectral regions in producing fluorescence, even if the specific exciting power, *i. e.*, the fluorescence excited per unit of *absorbed* energy, were in reality constant for all wave-lengths.

The determination of the relation between the specific exciting power and the wave-length of the exciting light is a problem of some interest, whose results possess also considerable significance on account of their bearing upon the theory of fluorescence. The present paper deals with the determination of this relation for eosin and resorufin.

The exciting light was furnished by a Nernst glower, which took the place of the slit of a large spectrometer. A narrow region in the spectrum thus formed was used in exciting the solution studied, and the intensity of fluorescence produced was measured by a spectrophotometer as the wave-length of the exciting band was varied.

The arrangement for exciting and observing fluorescence will be made more clear by inspection of Fig. 90. The light of the Nernst

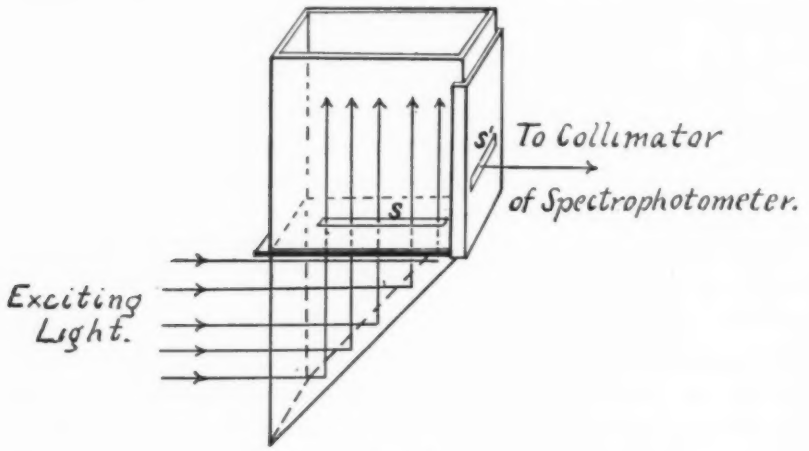


Fig. 90.

glower, after passing through the large spectrometer before mentioned, was reflected directly upward by a total reflecting prism as shown in the figure, and passed through a horizontal slit S into the cubical glass vessel which contained the solution to be studied. The spectrometer was adjusted so as to bring the spectrum in focus at the slit S. One vertical face of the cubical cell was covered with a sheet of metal containing a slit S' as shown in the figure. The exciting light passing through the slit S excited a narrow, vertical strip in the liquid to fluorescence, and this was observed through the slit S', in front of which the collimator slit of the spectrophotometer was placed. The comparison source for the spectrophotometer was an acetylene flame sliding upon a photometer track so that it could be set at different distances on the ground glass in front of the slit. This procedure makes it possible to keep

the slit width constant, and therefore eliminates the errors which might be introduced in measurements where the variation of intensity is great. The collimator slit of the spectrophotometer was broad and the instrument was set so as to measure the central part of the fluorescence band.

The Nernst glower which furnished the exciting light was attached permanently to the collimator tube of the large spectrometer, and in fact took the place of the slit of this instrument. The wave-length of the light used for excitation was varied by swinging the arm carrying the collimator and glower, the other portions of the spectrometer remaining fixed in position. At frequent intervals, corresponding to wave-lengths of the exciting light which differed only slightly from one another, the intensity of the fluorescence excited was measured by the spectrophotometer. The cell containing the fluorescent solution was then emptied and carefully cleaned and a piece of magnesium carbonate was mounted obliquely in the cell so as to reflect light from the slit S into the spectrophotometer. The intensity and range of wave-lengths of the light thus reflected were measured for each of the spectrometer settings previously used. Finally the absorption of a layer of the solution of known thickness was measured for some definite wave-length in the spectrum. By a separate series of measurements the relative reflecting power of the magnesium carbonate was determined throughout the region used.

The procedure in computing results was as follows: To correct for the unequal reflecting power of magnesium carbonate at different wave-lengths, the observed intensity, I_0, of the exciting light was divided by the reflecting power of magnesium carbonate for that particular wave-length. This correction reached approximately ten per cent. as its highest value. Using the values previously determined by us for the distribution of energy in the spectrum of the acetylene flame, we next determined the relative energy intensity of the light used for excitation as a function of the wave-length. It will be noticed that this procedure not only takes account of the difference in quality and energy distribution between the Nernst glower and the acetylene flame, but also eliminates any errors which might arise on account of selective transmission or other causes anywhere in the apparatus.

The center of the slit S' through which the fluorescence was absorbed was 8.2 mm. above the bottom of the cell containing the solution. On the average therefore the exciting light had passed through 8.2 mm. of solution before reaching the region whose fluorescence was measured by the spectrophotometer. The light available at this point to produce excitation was therefore less than that falling upon the face of the cell in the ratio of one to $e^{-0.82\alpha}$. It was therefore necessary to compute this factor $e^{-0.82\alpha}$ for each wave-length. In the case of eosin the solution was used the same that had been employed in determining the absorption curve given in our last paper for the more concentrated of the two solutions there studied. The value of α for each wave-length could therefore be read off at once from this curve. In the case of resorufin a different solution was used. Since, however, it has been shown that the form of the absorption curve is the same for all concentrations, it was sufficient to determine the absorption for one particular wave-length and then to reduce the values read from the curve of our last paper in a constant ratio.

Having computed in this way the intensity of the rays which actually reach the region in the solution that is under observation, and which are therefore available for producing excitation we must next compute the amount of energy actually absorbed in each case by multiplying $I_0 e^{-0.82\alpha}$ by α. Finally the absorbed fluorescence divided by the absorbed energy which produced it gave the quantity sought, that is, the intensity of fluorescence excited by unit quantity of absorbed energy of the particular wave-length in question.

In the case of eosin the observed data as well as the derived quantities corresponding to several steps in the computation are given in Table I. In the case of resorufin the same thing is shown graphically (Fig. 91). The observed points in each case are connected by full lines, while in the case of computed values the points are connected by broken lines. In curve *I* we have the intensity of the exciting light after reflection from magnesium carbonate. Curve *II* gives the energy intensity of the light actually reaching that part of the solution opposite the slit S'. The ordinates of curve *III* are obtained by multiplying each of the ordinates of

TABLE I.

Eosin.

1 λ	2 Intensity of Fluorescence.	3 Intensity of Exciting Light.	4 Reflecting Power of $MgCO_3$.	5 I_0 Corrected for Reflection.	Energy in C_2H_2 Spectrum.	7 I_0 (Energy.)	8 I_0e^{-ax}	9 $a.I_0e^{-ax}$	10 Specific Exciting Po
.479μ	2.2	8.25	102	8.08	1.15	9.3	7.0	2.45	0.9
.485	2.9	8.4	103	8.15	1.38	11.2	7.6	3.53	0.82
.491	4.1	8.3	104	7.98	1.59	12.7	8.4	4.24	0.97
.497	5.3	8.4	105	8.00	1.77	14.2	8.65	5.20	1.02
.501	6.3	10.1	108	9.37	1.90	17.8	10.1	6.98	.90
.509	8.6	8.9	111	8.00	2.13	17.1	8.12	7.37	1.17
.514	10.4	11.2	111	10.1	2.26	22.8	8.13	10.3	1.01
.521	11.0	11.0	111	9.9	2.40	23.8	5.60	9.9	1.11
.526	13.0	12.2	111	11.0	2.58	28.4	5.98	11.4	1.14
.534	17.0	12.0	110	10.8	2.90	31.3	9.76	13.8	1.23
.540	18.3	12.5	109	11.5	3.14	36.2	19.6	14.7	1.25
.547	11.0	12.2	108	11.3	3.4	38.4	31.0	8.07	1.37
.556	4.8	12.7	107	11.9	3.84	84.5	42.7	3.85	1.25

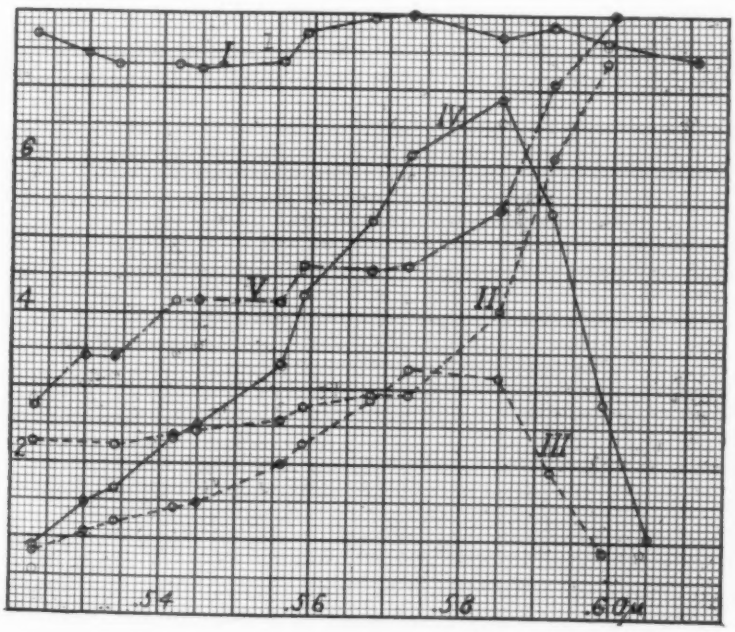


Fig. 91.

Resorufin.

curve *II* by α. Curve *III* therefore gives the energy actually observed from the exciting light for each wave-length. When the ordinates of curve *IV*, which shows the observed fluorescence, are

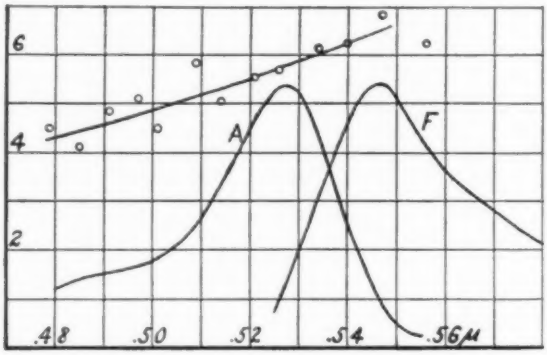


Fig. 92.

divided by the ordinates of curve *III* we have the quantity desired, namely, the fluorescence excited per unit of observed energy (curve *V*).

The results for eosin are shown in Fig. 92 and for resorufin in Fig. 93. In the case of the latter figure the values corresponding

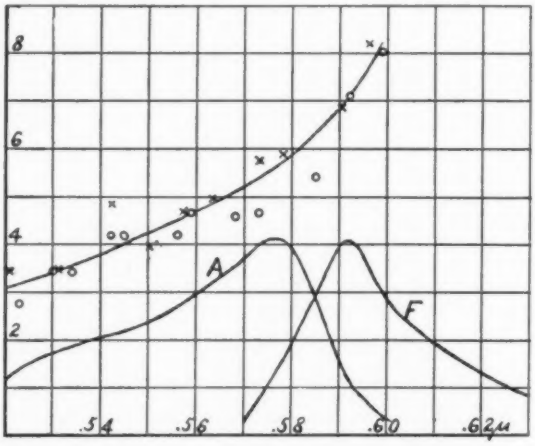


Fig. 93.

Resorufin. Intensity of fluorescence excited by different wave-lengths per unit of absorbed energy. The circles and crosses give the results of two independent sets of observations. Curve *A* gives the coefficient of absorption and curve *F* the energy distribution in the fluorescence spectrum.

to those shown in Fig. 91 are marked by circles. The crosses show the values obtained by another set of observations which are not here recorded in detail. The individual points on these curves show considerable erratic variation. In many cases these can be traced back to irregularities in the original data, doubtless due to some experimental errors. In making computations we have made no effort to eliminate these errors by smoothing the curves, but have taken each observation as it stood and carried through the work to the final result. Smooth curves have, however, been drawn among the computed points in Figs. 92 and 93. The data and results recorded here represent the best of a number of series of observations. While those not recorded gave more irregular results than here shown they all agreed in indicating the same general trend in the final curve.

In each of these two figures also we have plotted in the curves for the coefficient of absorption (A) and for the energy distribution in the fluorescence spectrum (F). It would seem reasonable to expect that the curve of specific exciting power might show some peculiarities either in the region of maximum absorption or in that of most intense fluorescence. It appears, however, that nothing of this kind occurs.

Before beginning these experiments we were of the opinion that either the specific exciting power would prove to be constant, so that the same quantity of absorbed energy would produce the same fluorescence regardless of its wave-length, or else that the effectiveness of the exciting light would prove to be greater for the shorter wave-lengths. The readiness with which fluorescence is excited in the ultra-violet spectrum made the latter view seem plausible. As it turns out neither of these views is in accord with the facts. We were unfortunately unable to extend the observations to the ultra-violet spectrum. It seems clear, however, that if we confine our attention to wave-lengths falling within the range of one absorption band, the light lying near the red side of the band is more effective in producing fluorescence than that lying on the violet side, and the change in the specific exciting power as we pass through the band is continuous, without any indication of anything selective in the neighborhood of the region of maximum absorption.

INFRA-RED ABSORPTION SPECTRA.

BY WILLIBALD WENIGER.

INTRODUCTION.

MANY investigators have examined the characteristics of absorption spectra, endeavoring to ascertain a possible systematic relation between absorption spectra and chemical constitution. That some relation exists is almost axiomatic in view of the many relations known to exist between chemical structure and other physical properties. With this end in view, all regions of the spectrum have been examined: the visible, the ultra-violet, and the infra-red; but the whole matter is still in a state of great confusion as can readily be seen by examining the summaries given in Kayser[1] and in Winkelmann.[2] This state of confusion, in spite of the excellent and more recent work of Coblentz,[3] indicated the need of a more detailed and if possible more systematic study than had heretofore been made, of some small part of the field. The part chosen for this investigation was the infra-red, and the substances first selected for examination were the liquid alcohols, acids, and esters, for besides permitting a study of homology and isomerism, the most promising lines of attack, these classes of substances also permit a study of the results of certain chemical reactions. Quite naturally these substances were supplemented by others whose desirability was recognized as the work progressed.

APPARATUS.

A general idea of the arrangement of the apparatus is given by Fig. 1. The radiation from a Nernst glower *A* was focused by the mirror *B* upon the slit *D* after passing through the absorption cell *C*. The cone of rays was made parallel by the mirror *E*, passed through

[1]Handb. d. Spectr., Vol. 3.
[2]Handb. d. Phys., Vol. 3.
[3]Investigations of Infra-red Spectra, Carnegie Inst., 1905.

the rock salt prism *F*, reflected from the plane mirror *G*, and focused by the mirror *H* upon the bolometer *I*. The bolometer was connected to a mirror galvanometer *J*, whose swings were photographed on a plate at *K*. The spectrometer was turned and the plate dropped by means of gears operated by the chronograph clockwork *L*. In order that the adjustments might be permanent, all of this

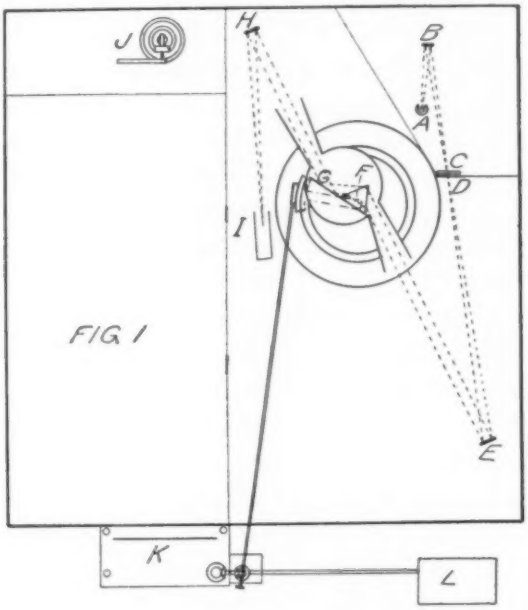


FIG. 1

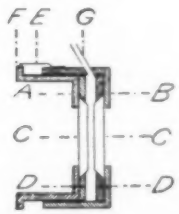


FIG. 2

Figs. 1–2.

apparatus, with the exception of the chronograph, was mounted on a solid brick pier with a large stone top.

A 98-volt, 0.8-ampere, D.C. Nernst glower was used as the source of radiation; for the sake of steadiness it was mounted in a cavity in a piece of fire brick. The current was supplied by storage

batteries and was kept at the rated value except when working beyond 10μ, when it was raised to 0.9 amp.

It was rather difficult to design a suitable absorption cell, as it was necessary to make one that would hold a few drops of some volatile liquid without marked evaporation for an hour and a half or two hours, the time needed for an examination of the liquid. The cell finally made was very satisfactory, inasmuch as a thin film of benzol remained in it for a day before evaporating. It consisted of two brass parts, *A* and *B*, Fig. 2, movable, one within the other, on a carefully cut no. 40 thread; each part carried a rock salt plate *C*, as shown, the plates being held in position by bevelled clamp rings, *D*, and screws. The rock salt plates were polished by hand in the usual manner with rouge on a surface of plant pitch and resin after being turned to size, bevelled to fit the clamp rings, and made plane parallel on a lathe.

The cell was filled by simply pouring a few drops of the liquid into B while in a horizontal position, and then screwing down *A* until the pointer *E* indicated the proper thickness of film on the flange *F*, which was graduated; the excess liquid was forced into a pipe *G* provided for the purpose. Upon opening the cell after an experiment it was found that if the liquid was hygroscopic it would generally attract enough moisture from the air to fog the salt plates while they were drying, while if the liquid was viscous, it would adhere to the plates for several hours in sufficient quantity to give traces of absorption bands. Hence it was made a rule to polish the plates whenever the cell was opened. Contamination of the liquids was carefully guarded against; the only substances with which they came into contact were the brass and the salt of the cell, and possibly a trace of rouge left on the edge of a plate after polishing.

The cell and a pair of salt plates of approximately the same thickness as those in the cell were mounted side by side upon a frame sliding upon horizontal ways so that either the one or the other could be brought before the slit. By getting the absorption due to a full cell and to the clear plates for the same wave-length, all corrections such as those due to absorption by the salt and selective reflection from its surface are done away with; the ratio of the two values found gives the per cent. transmission directly.

When put in the path of the radiation, the cell naturally becomes heated somewhat, but no provision need be made for cooling, as Coblentz[1] has shown that in general a change of as much as 20° C. from room temperature causes no change in the spectra.

The slit was 15 mm. in height and of adjustable width, 0.5 mm. being used in the region from 1 to 10μ, and 1 mm. for the remainder of the spectrum, where the energy was small. This widening of the slit does not, of course, involve a loss of accuracy, as the dispersion of rock salt is far greater for long wave-lengths than for shorter ones.

The spectrometer used was a large one of the fixed arm type specially designed for infra-red work by Professor C. E. Mendenhall. It was provided with a Warner and Swasey twelve-inch circle and an accurate worm and segment of worm wheel; the worm could be turned from the camera by means of a long rod bearing a micrometer head so graduated that the smallest division on it corresponded to a rotation of the prism through ten seconds of arc. The prism table was so constructed that all the adjustments required by the Wadsworth[2] mounting could be accurately made; it was set in hole, slot, and plane plates so that it could be removed entirely for convenience in carrying out the adjustment for minimum deviation, and was provided with a tin hood and several small dishes of sulphuric acid to dry the air surrounding the prism.

The rock salt prism was polished by Brashear and had these dimensions: refracting edge, 7 cm.; width of face, 5 cm.; angle, 60° 5.82′. To translate micrometer head readings into wave-lengths, a curve was plotted connecting angular rotation from the sodium line with wave-lengths, computations for the same being based on the indices of refraction of rock salt for different wave-lengths as given by Langley's[3] composite curve up to 10μ, and by Rubens and Trowbridge[4] beyond that point. For rough work a wave-length scale was made so that the position in the spectrum was indicated by the position of a mark on a string as the latter was wound up on the micrometer head. To check the accuracy of the

[1]Carnegie Institution, p. 106.
[2]Phil. Mag., 38, p. 344.
[3]Ann. Astrophys. Obs., I., p. 261, 1900.
[4]Am. J. Sci., V., p. 41, 1898.

adjustments, the carbon dioxide emission band in a Bunsen burner, and the two sylvite absorption bands were used; all were found accurately in place, the former at 4.4[1] and the latter two at 3.78 and 7.08.[2]

The mirrors *E* and *H* (Fig. 1) had focal lengths of 90 and 60 cm. respectively so that the 15-mm. slit gave a 10 mm. image. The curvature of the image was calculated and found to be negligible.

As required by the size of the mirrors used, the bolometer strips were made 10.5 mm. long from platinum foil 0.5 mm. wide, their resistances when soldered in place and smoked being respectively 5.660 and 5.669 ohms. This strip resistance, by Abbot's[3] method of calculation necessitates balance coils of 9.5 ohms each. These coils were wound non-inductively and in twin to equalize heating effects; they could be balanced by means of a shunt over a small part of one of them consisting of two parallel Ia wires connected by a movable mercury contact. The whole instrument was made as compact as possible, and, exclusive of the water jacket, measured about 20 cm. in length and 6 cm. in diameter. A large opening was left down the axis of the instrument so that a long focus microscope could be used to get the unshielded platinum strip in the focal plane of the mirror *H*.

An attempt was made to attain a high sensibility by enclosing the strips in a vacuum. It was found that the sensibility and steadiness on a given current increased at low pressures, but the high vacuum necessary could not be made to hold permanently. Vacua of one or two millimeters were at times held for a week or ten days, but the slightest jar would start a leak, and as the total volume exhausted was only about two cubic inches, a slight leak would immediately cause great disturbance, for at these low pressures the bolometer is extremely sensitive to pressure changes. The vacuum was finally discarded, but the rock salt window in front of the strips was retained to shut out air pulses.

The 0.5-mm. bolometer strip being placed at the focus of a mirror having a focal length of 60 cm., subtended an angle of a trifle less

[1]Paschen, Ann. d. Phys. (3), 53, p. 337, 1894.
[2]A. Trowbridge, Ann. Phys. u. Chem., 65, p. 612, 1898.
[3]Ann. Astrophys. Obs., I., p. 245, 1900.

than 3′ in the spectrum; this is equivalent to about 0.08μ at 1μ or to 0.5μ at 3.2μ, the region of least dispersion in the rock salt spectrum. The bolometer current was 0.08 amperes as a rule, the current being supplied by three storage cells in parallel.

The galvanometer was of the four-coil astatic type. In order to enable the use of a light system as well as to avoid the use of unwieldy shielding, it was sought to make the instrument as small as possible; consequently the external diameter of the coils was limited to 2 cm. To match the bolometer, a galvanometer resistance of about 5 ohms is best. Using Abbot's[1] formula to determine the sizes and lengths of wire that would give the maximum field strength under these conditions, two coils of respectively 16 and 25 ohms were calculated. In order to give an idea of the effect of varying the different quantities in the formula, all the results are put down in Table I. The coils marked * are of course the best under the limitations set. The 16 ohm coils were wound and all connected in parallel.

The galvanometer shielding consisted of three concentric soft

TABLE I.

Galvanometer coils computed by means of Abbot's formula. R, resistance in ohms; L, length of wire in cms.; H, external radius of coils in cms.; F, force at center of coils; W, size of wire, B & S. gauge. Subscripts—1 refer to inner section of coil, 2 to middle, 3 to outer.

W_1	W_2	W_3	R_1	R_2	R_3	L_1	L_2	L_3	H_1	H_2	H_3	F_1	F_2	F_3	F
40	36	34	12	8	5	369.1	622.3	780.0	.4868	.6099	.7816	824	485	362	1671
40	36	34	10	5	7	307.6	622.3	865.9	.3994	.6026	.7850	743	527	418	1688
40	36	34	7	8	10	215.3	622.3	1237.	.3684	.5923	.8442	607	569	514	1691
40	36	32	7	8	10	215.3	622.3	1967.	.3684	.5923	1.032	607	569	627	1803
40	36	32	11	8	6	338.4	622.3	1180.	.4984	.6059	.9154	785	516	636	1937*
40	34	30	8	5	3	246.1	618.5	938.1	.3795	.6495	.9676	655	475	311	1441*
40	34	30	8	5.5	2.5	246.1	680.4	781.7	.3795	.6649	.9374	655	520	250	1425
36	34	32	8	5	3	622.3	618.5	590.1	.5665	.7273	.8680	826	319	201	1346
36	34	30	8	5	3	622.3	618.5	938.1	.5665	.7273	1.004	826	319	199	1344
40	36	30	8	4.5	3.5	246.1	350.1	1095.	.3795	.5271	.9646	655	356	410	1421

[1]Ann. Astrophys. Obs., I., p. 248.

steel hollow cylinders of dimensions computed by the formulæ of Dubois and Wills[1] to give the maximum shielding; in addition there was within the inner hollow cylinder a solid cylinder of Swedish iron split lengthwise, the galvanometer coils being mounted directly in holes cut into the plane faces of the half cylinders. The inner hollow cylinder was provided with a plate glass top to shut out air draughts.

The astatic system consisted of two sets of tungsten steel magnets, four magnets to a set, mounted on a thin glass rod. The mirror on the system was about 3 mm. in diameter and was obtained by chipping the silvered concave surface of a 0.25 dioptric spectacle lens. To get rid of mechanical tremors, the whole system had to be made quite heavy—5.6 mg. To avoid cutting holes in the shield the system was illuminated from above by means of two small, plane mirrors and a horizontal A.C. Nernst glower, the glower being enclosed in a slotted brass tube. The glower and the photographic plate were of course at conjugate foci of the galvanometer mirror, the distance from the mirror to the plate being 170 cm.

The sensibility of the galvanometer on a complete period of 4 sec. was 5×10^{-10}, but frequently a 6-sec. period was used. With a period of 4 sec. or more the galvanometer was practically dead-beat. The deflections could be cut down by a combination of series and parallel resistances, the entire circuit being made of copper to eliminate thermal electromotive forces. The sensibility of the entire bolometer-galvanometer system when the galvanometer had a period of 4 sec. and the bolometer carried the usual current of 0.04 ampere per strip, was such that if there had been no series or parallel resistance in circuit with the galvanometer, a candle at a distance of a meter from the bolometer would have given a deflection of 30 cm. on a scale one meter from the galvanometer.

The camera consisted of a wooden box about three feet high built up around four standards, the galvanometer light being admitted through a horizontal slit 1 mm. wide. The plate carrier, holding a plate 11.5×14 inches, was guided by two of the standards, one of which was provided with a thread of 12 mm. pitch; a nut on the carrier engaged this thread and allowed the carrier to drop uniformly as the threaded standard was turned.

[1]Ann. d. Phys., II., p. 78, 1900.

This standard and the worm on the spectrometer were geared together so that vertical positions on the plate could be interpreted as angular displacements of the spectrometer and hence as wave-lengths. For the region from 3–4μ, the most condensed interval in the rock salt spectrum, the vertical displacement was 1 cm. The plate was lowered at the rate of 0.5 cm. per min., the speed of the whole system being regulated by the clockwork of a chronograph.

Method of Observation.

The following method of procedure was found to be the most rapid means of getting good consistent results. To make sure that no adjustment of the prism system had been disturbed, the sodium line was thrown on the bolometer both before and after the examination of each substance. After this preliminary test both of the Nernst glowers were started and three spot records made on the photographic plate: one a zero spot obtained by cutting off all radiations by means of a screen in front of the slit; another a clear plate transmission spot obtained by pulling the clear plate in front of the slit; lastly a transmission spot through the cell. The motor was then started and allowed to run for a few minutes, a trace of the transmission through the cell being obtained during this time; the motor was then stopped and zero and clear plate transmission spots again taken. This process was continued throughout the entire spectrum, the sensibility of the galvanometer being changed at some of the stops to obtain suitable deflections. Four curves were usually taken on each plate, two starting near one end of the plate and two near the other. Two curves were taken of each substance, sometimes on the same day, sometimes on different days.

After a plate was developed, all the zero points of any one set and all the clear plate points were connected by ink lines. For any one wave-length, the ratio of the distances zero line to cell line, and zero line to clear plate line, gave the per cent. transmission. For convenience in reading a plate it was laid on a frame at an angle of 45° with the horizontal, light being reflected through it from a sheet of white paper. Along the left hand edge of the frame slid a counterbalanced T square whose arm was graduated

so that each division corresponded to a vertical drop of the plate of 0.1 μ. A celluloid triangle with a millimeter scale graduated on a bevelled edge slid along the T square and served to measure the ratio distances, the actual ratios being read off on a slide rule. Curves were then plotted using per cent. transmission as ordinates and wave-lengths in μ's as abscissas.

To avoid confusion only one curve has been reproduced for each substance (Plates I, II, and III, p. 420). But to give an idea of how closely the curves check one another, both curves are given for isoamyl butyrate (no. 31) and isoamyl propionate (no. 30). The first of these is a fair sample of the way in which two curves checked when the thickness of the film was the same in the two cases, and the second illustrates the difference in appearance of the curves due to a difference in film thickness; some of the bands run together into a deep band, but the individual minima can be distinguished if the film is not too thick. The thickness of the film used in each case is given in Table II.

To give an idea of the actual appearance of the photographic plate, a small part of one is reproduced without reduction in Fig. 3 (Plate I, p. 420).

Sources of Error.

In interpreting the curves, use has been made of the relative depths of the absorption bands as well as of their positions, so that errors affecting either the depth or the position of a band must be considered. As the chief sources of error may be mentioned: Variation in brilliancy of the Nernst glower, bolometer drift and unsteadiness, inaccuracy in the drawing of the clear plate transmission curve, impurity of spectrum due to finite widths of slit and bolometer.

Variation in brilliancy of the Nernst glower will affect the transmission curves of both the clear plate and the cell in the same ratio, so that no error would be caused by such a variation if it were possible to get simultaneous traces of the transmission through the clear plate and through the cell. In the trace on the photographic plate, however, the clear plate transmission is represented only by dots taken at intervals. A sudden change in brilliancy between two dots might therefore affect both the depth and the position of a

TABLE II.

Curve No.	Substance.	Sample. b.p. °C.	Sample. Pres. mm.	Thickness of film, mm.	Formula.
1	Methyl alcohol	63.7	726.5	0.01	CH_3OH
2	Ethyl alcohol	77.0	728.8	0.01	CH_3CH_2OH
3	Primary propyl alc.	95.9	726.2	0.01	$CH_3CH_2CH_2OH$
4	Primary butyl alc.	115.9	743.1	0.01	$CH_3(CH_2)_2CH_2OH$
5	Primary amyl alc.	136.8	743.9	0.01	$CH_3(CH_2)_3CH_2OH$
6	Sodium alcoholate			0.005	CH_3CH_2ONa
7	Isobutyl alcohol	105.5	740.3	0.01	$(CH_3)_2CHCH_2OH$
8	Isoamyl alcohol	130.0	732.6	0.01	$(CH_3)_2CHCH_2CH_2OH$
9	Allyl alcohol	95.5–95.6	747.0	0.01	CH_2CHCH_2OH
10	Capryl alcohol	174.0–176.0	729.0	0.01 0.01	$CH_3(CH_2)_5CHOHCH_3$
11	Secondary propyl alc.	81.6	739.9	0.01	$CH_3CHOHCH_3$
12	Secondary butyl alc.	98.9	740.3	0.01	$CH_3CH_2CHOHCH_3$
13	Tertiary amyl alc.	101.0–102.0	738.7	0.01	$CH_3CH_2COH(CH_3)_2$
14	Butyric acid	161.5	743.0	0.03	$CH_3CH_2CH_2COOH$
15	Methyl acetate	57.1	733.0	0.02	CH_3COOCH_3
16	Methyl propionate	77.0–79.0	737.5	0.02	$CH_3CH_2COOCH_3$
17	Methyl butyrate	102.0–102.5	742.0	0.02	$CH_3CH_2CH_2COOCH_3$
18	Methyl isovalerianate	116.7	742.0	0.02	$(CH_3)_2CHCH_2COOCH_3$
19	Isobutyric acid	152.7–153.0	743.0	0.03	$(CH_3)_2CHCOOH$
20	Ethyl acetate	75.0	744.4	0.02	$CH_3COOCH_2CH_3$
21	Ethyl propionate	98.0	737.5	0.01	$CH_3CH_2COOCH_2CH_3$
22	Ethyl butyrate	119.5–119.9	742.0	0.02	$CH_3CH_2CH_2COOCH_2CH_3$
23	Methyl isobutyrate	92.0–93.0	742.0	0.01	$(CH_3)_2CHCOOCH_3$
24	Methyl hexyl carbinol acetic ester	193.0	746.5	0.01	$CH_3COOCHCH_3(CH_2)_5CH_3$
25	Isobutyl acetate	115.8–116.3	744.5	0.03	$CH_3COOCH_2CH(CH_3)_2$
26	Butyl butyrate	164.0–165.0	741.0	0.01	$CH_3CH_2CH_2COOCH_2(CH_2)_2CH_3$
27	Isoamyl isobutyrate	168.0–168.5	742.5	0.01	$(CH_3)_2COOCH_2CH_2CH(CH_3)_2$
28	Isoamyl formate	123.0	746.0	0.02	$HCOOCH_2CH_2CH(CH_3)_2$
29	Isoamyl acetate	138.5–138.7	744.5	0.02	$CH_3COOCH_2CH_2CH(CH_3)_2$
30	Isoamyl propionate	160.0	743.0	0.01	$CH_3CH_2COOCH_2CH_2CH(CH_3)_2$
31	Isoamyl butyrate	177.0	745.4	0.01	$CH_3CH_2CH_2COOCH_2CH_2CH(CH_3)_2$

TABLE II.—*Continued.*

Curve No.	Substance.	Sample. b.p. °C.	Sample. Pres. mm.	Thickness of film, mm.	Formula.
32	Isoamyl isovalerianate	190.0	741.0	0.03	$(CH_3)_2CHCH_2COOCH_2CH_2CH(CH_3)_2$
33	Ethylene glycol	190.0	734.5	0.01	$(CH_2OH)_2$
34	Propylene glycol	181.0–182.0	738.0	0.01	$CH_2OHCHOHCH_3$
35	Glycerin	(m.p.) 17–18		0.01	$CH_2OHCHOHCH_2OH$
36	Acetaldehyde	21.5–22.0	742.0	0.005	CH_3CHO
37	Ethyl oxalate	116.5	120.0	0.01	$COOHCOOCH_2CH_3$
38	Ethyl malonate	193.0–195.0	738.0	0.01	$COOHCH_2COOCH_2CH_3$
39	Ethyl succinate	215.0	736.1	0.02	$CH_2COOHCH_2COOCH_2CH_3$
40	Diethyl oxalate	181.9	741.0	0.01	$COOCH_2CH_3COOCH_2CH_3$
41	Diethyl succinate	213.0	736.1	0.02	$CH_2COOCH_2CH_3CH_2COOCH_2CH_3$

band. Any great error due to this cause is excluded by the fact that two records were always taken for each substance; in case of disagreement the doubtful portion was gone over a third time.

Bolometer drift, through present, was at all times small; it was kept track of by means of the zero spots taken from time to time. As all measurements were made from a smooth curve joining these spots, the effect of drift is practically eliminated.

An error may have been, and probably was made, in joining the points giving the transmission through the clear plate, but the variations of the curve as drawn from the true curve could not have been great in any case as the points on the curve were taken close together, and as, in addition, the form of the true curve was known quite well from direct traces of it made occasionally.

The correction for finite width of slit and bolometer,[1] though appreciable, has not been applied to the curves as plotted since it would affect all similar curves to approximately the same extent at the same points in the spectrum; the comparison of the origina curves leads to the same results as would the comparison of the corrected curves.

[1]Summarized in Preston's Heat, last edition, p. 606.

The Materials Used.

All the substances used were either synthesized or taken from stock and distilled shortly before they were examined. If several days elapsed between the time of preparation and the time of examination, the liquids were kept in glass stoppered bottles in the dark. The thermometer used was compared with one having a Reichsanstalt certificate. The boiling points of the various substances and the corresponding pressures are given in Table II.

The Alcohols were all taken from stock bottles, dried for several days over anhydrous copper sulphate, and distilled over sodium. The solution of sodium alcholate in alcohol was obtained by dissolving sodium in absolute alcohol until the whole mass was just ready to become solid; the sample was tested immediately after it was made.

The Glycols.—Ethylene glycol was taken from stock (Schuchardt), dried over anhydrous calcium chloride, and distilled. Propylene glycol was made by Morley's[1] method, which consists in dissolving lye in glycerin, heating and distilling; this was the only substance examined that was not colorless; it had a pale yellow tinge.

Glycerin.—The purest glycerin obtainable was frozen and the crystals filtered off, the process being repeated twice; melting point 17–18°.

The Acids were taken from stock (Schuchardt), dried over anhydrous calcium chloride and distilled.

The Esters.—All the monobasic esters except two were made from the pure acids and alcohols by the hydrochloric acid method. A mixture of the proper acid and alcohol, containing a large excess of the one that happened to be the more plentiful, was saturated at 0° C. with dry hydrochloric acid; the action was completed by boiling for about fifteen minutes with a reflux condenser; the ester was separated by shaking the mixture with a saturated solution of calcium chloride or with granular calcium chloride, and was then dried and fractionated.

The two isovalerianates were taken from stock (Schuchardt), dried over calcium chloride and distilled.

Of the more complex esters, diethyl oxalate, ethyl malonate and

[1]Chem. Soc. Journ., 47, p. 132.

ethyl succinate were taken from stock, dried and distilled. Ethyl oxalate was made by heating anhydrous oxalic acid and absolute alcohol slowly under diminished pressure. The mixture was cooled and later fractionated in a partial vacuum. Diethyl succinate was made by the hydrochloric acid method from the pure acid and alcohol.

Acetaldehyde.—Some of Kahlbaum's product was distilled with dilute sulphuric acid, dried over anhydrous sodium sulphate and distilled. As acetaldehyde rapidly polymerizes in part to paraldehyde at room temperature, it was examined immediately after being distilled.

DISCUSSION.

As stated in the introduction, the investigation was begun with a study of the effects of homology and isomerism. Of these two, homology is somewhat the simpler. In any study of the relation between chemical composition and physical properties it is customary to assume that similarities in chemical constitution cause similarities in physical properties. All homologous compounds are similar in constitution, for by definition, two successive members of a homologous series must be similar in their properties, and must differ by CH_2, a hydrogen atom in one having been replaced by a methyl group in the other. Hence regularities in the spectra of the members of such a series may be expected.

Among isomers, however, the case is somewhat different. Isomeric compounds are defined as compounds that have the same percentage composition and the same molecular weight, but different properties. Since isomers are essentially different in structure, differences in the spectra are to be expected; but some isomers differ radically in structure while others differ only slightly, and on the basis of the original assumption a corresponding relative difference in the spectra is to be expected. From a study of those isomers that are somewhat closely related in structure it seemed probable that a definite correlation might be obtained between certain groups or linkages and certain bands. Such correlations, it seemed likely, might afterwards be corroborated and extended by following up the results of a chemical reaction, and by studying related compounds. This is, in outline, the scheme that has been followed in the selection of the substances and in their comparison.

The alcohols were the first substances selected for investigation. Those with a single atom of oxygen fall into three classes having the general formulæ $C_nH_{2n+1}OH$, $C_nH_{2n-1}OH$, and $C_nH_{2n-3}OH$. The members of the first class, which includes most of the specimens examined, are further distinguished as primary, secondary, or tertiary, according as the hydroxyl group is attached to a CH_2, to a CH, or to a C.

A general idea of the relations of the various alcohols of the first class to each other is given by the accompanying table.

Methyl CH_3OH				
Ethyl CH_3CH_2OH				
Normal or primary propyl $CH_3.CH_2.CH_2OH$			Secondary propyl $CH_3CH_3>CH.OH$	
Normal butyl $CH_3(CH_2)_2CH_2OH$	Isobutyl $CH_3CH_3>CH.CH_2OH$		Secondary butyl $CH_3CH_2CH_3>CHOH$	Tertiary butyl $CH_3CH_3CH_3>COH$
Normal amyl $CH_3(CH_2)_3CH_2OH$	(Active amyl) $CH_3CH_2CH_3>CH.CH_2OH$	Isoamyl $CH_3CH_3>CH.CH_2.CH_2OH$	(Secondary amyl) $CH_3(CH_2)_2CH_3>CHOH$	Tertiary amyl $CH_3CH_3CH_2CH_3>COH$

Columns in this table represent homologous series and any alcohogives rise to the next succeeding one in the same column if a hydrol gen atom be taken from a methyl (CH_3) group and replaced by another methyl group. Rows in the table represent isomers, but the change in structure is different for different pairs of consecutive members. Isomers from the first and second columns, for example, differ only slightly from one another chemically; the difference in structure exists entirely in the hydrocarbon part of the compounds, the linking of the characteristic hydroxyl group remaining unchanged. The same is true of isomers of the first and third columns but those from the first and fourth or first and fifth differ more materially since in these the linking of the hydroxyl is changed.

The table is complete as far as it goes except that three of the amyl alcohols, which were not used, have been omitted to save

space. Capryl alcohol, one of the higher secondary alcohols, belonging two rows below secondary amyl, was examined in addition to those put down in the table. Those alcohols that are included in parentheses were not available.

The saturated monobasic acids, $C_nH_{2n+1}COOH$, are divided, just as the alcohols are, into primary, secondary, and tertiary compounds, an acid being primary if the carboxyl group, COOH, is attached to CH_2, secondary if attached to a CH, and tertiary if attached to a C. The primary acids form the series:

$HCOOH$ formic,
CH_3COOH acetic,
CH_3CH_2COOH propionic,
$CH_3CH_2CH_2COOH$ butyric,
$CH_3(CH_2)_2CH_2COOH$ valeric,
$CH_3(CH_2)_3CH_2COOH$ caproic.

Of these Coblentz[1] has examined acetic, valeric, and caproic, and in the present investigation, butyric has been added.

Analogous series of iso, secondary and tertiary acids also exist, of course, but of these only one specimen could be obtained, the so-called isobutyric, which is really a secondary acid as shown by its formula (Table II.).

The esters are salt-like derivatives of the various acids and alcohols, and hence a great many different ones exist, offering a correspondingly large number of homologous series and isomers. The esters examined were for the most part those obtained by the interaction of primary or iso alcohols with primary acids. The esters formed by the interaction of the primary alcohols and the primary acids may be arranged for convenience in tabular form as shown on page 403.

The members of any column, representing the combinations of some one alcohol with a series of acids, evidently form a homologous series. So also do the members of a row, for each row shows the results of combining some one acid with a series of alcohols. Those esters lying on lines that might be drawn in the diagram slanting from the right on the top to the left below, as, *e. g.*, ethyl formate and methyl acetate, or propyl formate, ethyl acetate and methy propionate, illustrate a particular kind of isomerism, the isomer-

[1]Carn. Inst., pp. 209–215.

ism being due to the successive transfer of a methyl group from the basic to the acid part of the compounds.

Methyl formate $HCOOCH_3$	**Ethyl formate** $HCOOCH_2CH_3$	**Propyl formate** $HCOO(CH_2)_2CH_3$	**Butyl formate** $HCOO(CH_2)_3CH_3$	**Amyl formate** $HCOO(CH_2)_4CH_3$
Methyl acetate CH_3COOCH_3	**Ethyl acetate** $CH_3COOCH_2CH_3$	**Propyl acetate** $CH_3COO(CH_2)_2CH_3$	**Butyl acetate** $CH_3COO(CH_2)_3CH_3$	**Amyl acetate** $CH_3COO(CH_2)_4CH_3$
Methyl proprionate $CH_3CH_2COOCH_3$	**Ethyl proprionate** $CH_3CH_2COOCH_2CH_3$	**Propyl proprionate** $CH_3CH_2COO(CH_2)_2CH_3$	**Butyl proprionate** $CH_3CH_2COO(CH_2)_3CH_3$	**Amyl proprionate** $CH_3CH_2COO(CH_2)_4CH_3$
Methyl butyrate $CH_3(CH_2)_2COOCH_3$	**Ethyl butyrate** $CH_3(CH_2)_2COOCH_2CH_3$	**Propyl butyrate** $CH_3(CH_2)_2COO(CH_2)_2CH_3$	**Butyl butyrate** $CH_3(CH_2)_2COO(CH_2)_3CH_3$	**Amyl butyrate** $CH_3(CH_2)_2COO(CH_2)_4CH_3$
Methyl valerianate $CH_3(CH_2)_3COOCH_3$	**Ethyl valerianate** $CH_3(CH_2)_3COOCH_2CH_3$	**Propyl valerianate** $CH_3(CH_2)_3COO(CH_2)_2CH_3$	**Butyl valerianate** $CH_3(CH_2)_3COO(CH_2)_3CH_3$	**Amyl valerianate** $CH_3(CH_2)_3COO(CH_2)_4CH_3$

A similar square array of esters can be made by combining the iso acids with the primary alcohols; another by combining the iso alcohols with the primary acids; another by combining the secondary acids with the primary alcohols, etc. Each such array would give rise to the two kinds of homologous series and to the kind of isomerism mentioned above. In addition, the substances occupying the same position in the different square arrays might be compared, all such substances being isomers of the primary—iso, primary—secondary, etc., types mentioned in connection with the alcohols. The preparation and study of all of these compounds is, however, unnecessary, as will be seen when the spectra of a few of them are compared.

To facilitate the comparison of the curves, related substances have been plotted as nearly as possible in the same order as the formulas tabulated above. In the esters the scheme of the square array has been followed except that the normal compounds have in some instances been replaced by the corresponding iso compounds. If, to economize space, any substance has been plotted out of its regular order, the fact is indicated by a heavy border. To aid in finding the curves, they have all been numbered in the order in which they appear on the sheets.

EFFECT OF ISOMERISM.

Primary-iso isomerism in the alcohols; this includes alcohols that differ in the hydrocarbon part but not in the linking of the hydroxyl. Two pairs of these isomers have been examined: butyl (no. 4) and isobutyl (no. 7), and amyl (no. 5) and isoamyl (no. 8). The three absorption regions from about 3.0–3.5, 6.5–7.5 and 9–10μ look very much alike in each primary and its isomer. In butyl and isobutyl the first absorption region has two bands, the first occurring at 3μ in both, and the second at 3.5 in the primary and 3.4 in the iso; the second region also has two bands, 6.9 and 7.2, alike in both; the third region has one band at 9.6 in both. There is also a band at 10.5 in the normal and 10.4 in the iso. The region between the second and third absorption regions has two minor bands in the primary and only one in the iso. Beyond 11μ the spectra are dissimilar.

In amyl and isoamyl the location of bands in the first region is identical to that in the butyls; the second region has two bands, 6.9 and 7.3, alike in both; the third region has two bands, 9.6 and 9.9 in amyl, and 9.5 and 9.9 in isoamyl. There is also a band at 10.3 in both. The region between the second and third main regions has three minor bands in the normal and two in the iso. Beyond 11μ the spectra are dissimilar.

The change from primary to iso therefore leaves the three main regions unchanged except for the shift of the 3.5 band to 3.4. In the region between the second and third absorption regions the iso alcohol has fewer minor bands than the primary. The regions beyond 11μ differ.

Primary-secondary isomerism in the alcohols; in these isomers the linking of the hydroxyl group is changed from CH_2OH to CHOH. Two pairs of these alcohols have been examined: Primary and secondary propyl (nos. 3 and 8), and primary and secondary butyl (nos. 4 and 9). The three absorption regions that were noted in the primaries before 10μ change their appearance somewhat in the secondaries. The first region is situated between 3 and 3.5μ in both the primaries and the secondaries, and shows two bands in each; the second region lies between 6.5 and 7.5μ in both, but has two bands in the primaries and three in the secondaries; the third region occurs between 9 and 10 in the primaries and between 8.5 and 9.5 in the secondaries. Several deep bands also appear in the secondaries beyond 10μ. In detail, the bands at 3.0 and 6.9 are again unchanged, and 3.5 again goes to 3.4. In place of a minor band at 6.1 in the primaries there is in both cases a much deeper one at 5.9 in the secondaries. The 7.2 band does not shift in the propyls but goes to 7.3 in secondary butyl. A new deep band exists at 7.7 in secondary propyl and at 7.6 in secondary butyl. The 8.2 band in primary propyl still exists in secondary propyl, but the 8.0 band in primary butyl has disappeared in secondary butyl. If the two absorption regions from 9–10 in the primaries and from 8.5 to 9.5 in the secondaries can be correlated, it means that the band near 9.6 in the primaries corresponds to that near 9.1 in the secondaries; in other words the band near 9.6 in the primaries has shifted by 0.5μ toward the shorter wave-lengths in the secondaries.

Another new band exists near 9.8 in the secondaries, being much deeper in the more complex compound. The band at 13.0 is not shifted in the propyls, but goes from 13.1 to 13.0 in the butyls. The change from primary to secondary, therefore, shifts more bands in the compounds richer in CH_2; more characteristic still is the appearance of the two new bands near 7.6 and 9.8 and the shift of the 9.6 band by 0.5μ toward the shorter wave-lengths in both secondary propyl and butyl.

Primary-tertiary isomerism in the alcohols; in these alcohols the linking of the hydroxyl is changed from CH_2OH to COH. Only one pair of these alcohols could be obtained: primary and tertiary amyl (nos. 5 and 13). The absorption regions between 3 and 4μ are again similar; the second region, near 7μ, has three bands in the tertiary in place of two, the three bands being separated somewhat farther from each other than in the secondaries where they also occur; the third region occurs between 9 and 10μ in the primaries and between 8 and 9 in the tertiary; beyond this region, the spectrum of the tertiary is more cut up than in the primaries or secondaries. In detail the bands at 3.0, 6.9, 7.3, 13.0, are unchanged; a weak band at 6.1 is found in the tertiary where there is none in the primary; a band appears at 7.9 and another disappears at 8.3, which may possibly indicate a shift. If the third absorption regions in the primary and the tertiary can be correlated, the 9.6 bands must be regarded as having shifted to 8.6; the fact that this shift from primary to tertiary is just double the shift of the same band from the primaries to the secondaries, strengthens the belief that the regions compared are really analogous. There is, to be sure, a band at 9.6 in tertiary amyl which may be due to a weakening of the deep band found at the same place in the primaries, but judging by the general similarity of the spectra, it seems best to correlate the 8.6 band in the tertiary with the 9.6 band in the primaries as indicated above. With this interpretation, the most noticeable changes in these isomers are the appearance of the new band at 7.9 and the shift of the 9.6 band by 1.0μ toward the shorter wave-lengths.

Primary-secondary isomerism in the acids. Data have been obtained on one pair of these acids, butyric and isobutyric (nos. 14

and 19), and Coblentz[1] has examined another pair, caproic and isocaproic, which may be compared somewhat more closely than he has done. Isobutyric acid is really a secondary acid, as mentioned before, and as shown by its formula in Table II. These acids show the following minima:

Butyric,	3.6	5.9	7.1	7.9		9.3	10.6	12.9
Isobutyric,	3.6	5.9	7.1	8.0	8.5	9.2	10.8	12.3

The most conspicuous change evidently is the appearance of two lines at 8.0 and 8.5 to take the place of the one at 7.9. Coblentz's curves for caproic acid, $CH_3(CH_2)_3CH_2COOH$, and isocaproic acid, which is really a secondary acid, $(CH_3)_2CH.CH(CH_3)COOH$, show a very similar behavior, as can be seen from their minima:

Caproic,	3.5	5.9	7.0	8.0		9.1	10.3	11.6	12.5
Isocaproic,	3.5	5.9	7.0	7.8	8.3	9.1	10.7		12.2

These acids therefore indicate that up to 12μ their spectra are very similar except in the region near 8μ where one band occurs when the carboxyl is linked to a CH_2 and two when linked to a CH.

Primary-secondary isomerism in the esters. Two pairs of these isomers are found in methyl butyrate and methyl isobutyrate (nos. 17 and 23), and isoamyl butyrate and isoamyl isobutyrate (nos. 31 and 27). In the methyl isomers, passing from normal to iso, the band at 4.4 goes to 4.2, that at 5.0 to 4.9, and that at 9.2 to 9.3; the normal compound has a single band in the 8μ region (8.4), while the iso compound has two (8.4 and 8.7). In the isoamyl isomers, similarly, the band at 4.3 goes to 4.2, that at 4.8 to 4.6, that at 9.2 to 9.3, and that at 8.5 into two at 8.4 and 8.6. It will be remembered that the change from primary to secondary acid also caused two bands to appear in place of one in the 8μ region; this splitting persists in the corresponding esters.

Isomerism in the esters due to shifting a CH_2 group from the basic to the acid part of the compound. Of this there are four illustrations:

1. Ethyl acetate (no. 20) and methyl propionate (no. 16).
2. Ethyl propionate (no. 21) and methyl butyrate (no. 17).
3. Isoamyl formate (no. 28), isobutyl acetate (no. 25), ethyl butyrate (no. 22), and methyl isovalerianate (no. 18).

[1]Carn. Inst., pp. 211, 212, 101.

4. Isoamyl propionate (no. 30) and butyl butyrate (no. 26).

On comparing these spectra in detail it appears that the shifting of the CH_2 can be correlated with no definite shift of any line or series of lines. This may mean that in this case the lines present depend on the groups present and not on their linking, or it may mean that the change made is too small to be noticed in so complex a molecule. Since compounds far apart, isoamyl formate and methyl isovalerianate, have been examined, four groups having been shifted from one side to the other in these compounds, it seems that the former view must be accepted.

To sum up: All the alcohols have bands at 3.0 and 6.9; the change from primary to iso causes a number of small shifts, the number being larger in compounds poor in CH_2; the secondary alcohols have a new band near 7.6 and the tertiaries have a corresponding one at 7.9; the change from primary to secondary causes a weakening of the bands in the 8μ region, and the change to tertiary causes a further weakening; a deep band appears at 9.6 in the primaries, is shifted to 9.1 in the secondaries, and to 8.6 in the tertiaries. The isomeric acids show great similarity in their spectra, the main point of difference being the fact that in the primaries there is a single line in the 8μ region, while in the secondaries there are two. The isomeric esters, for the same difference in structure, show the same difference in bands as the acids, indicating that some bands in the esters depend on the structure; on the other hand the fact that no marked change is caused by shifting CH_2 groups from the acid to the basic parts of the compound, indicates that certain other bands depend merely on the presence of certain groups; still, the change in chemical properties caused by this shift is relatively slight, so that comparisons of the different spectra show that the greater the difference in structure between isomers, the greater the difference in their spectra. This substantiates the conclusions of Julius[1] and of Coblentz, who found that a change in structure causes a change in the spectra.

EFFECT OF HOMOLOGY.

Homology in the primary alcohols. Five primary alcohols (nos. 1 to 5) were examined. In all the alcohols there are three deep

[1] Verh. Konikl. Akad., Amsterdam, Vol. 1, No. 1, 1892.

absorption regions before 10μ as was mentioned when discussing isomers. In the primary alcohols the first of these regions is occupied by one band in the lower members of the series and by two in the upper; the same is true of the second region. The space between the second and third regions is occupied by several minor bands whose number and depth increase in the higher members of the series. Beyond 10μ there is no more marked similarity. In detail, the 3μ band is constant in all, and the 3.5μ band is constant in the higher members, being absent in methyl and ethyl. There is a minor band at 4.9 in methyl, 5.2 in ethyl, 5.5 in propyl, 5.6 in butyl, and not observable in amyl; it is strongest in methyl and gets weaker as it shifts to the longer wave-lengths Another minor band behaves very much like this one: it occurs at 5.9 in methyl, 6.0 in ethyl, 6.1 in propyl, 6.1 in butyl, and disappears in amyl. The 6.9 band is practically constant, as is also the 7.2 band after it appears. The deepest band in the third absorption region is at 9.9 in methyl and at about 9.6 in the rest, showing a shift in the lower members of the series. A small band appears at 10.6 in ethyl, 10.4 in propyl and butyl, and 10.3 in amyl. Beyond this there is a band at about 13μ in all except methyl, where there is one at 13.3; but it is doubtful whether these can be correlated, as the general configuration of the spectra is not at all alike in this region. From the preceding it is seen that the bands that shift move towards the 9μ region from each side as the series is ascended, the shift being greater between the lower members.

Before leaving the primary alcohols attention must be called to the difference that exists between Coblentz's[1] curve for ethyl alcohol and mine (no. 2). The minima given in his curve fall at about 3.4, 7.3, 9.6, 11.4, 12.6, whereas mine fall at 3.0, 7.0, 7.2, 9.3, 9.6, 11.3, 12.5, 13.0. His curve shows no band at 3.0 at all, while in the present investigation this band was found in all the alcohols without exception. He mentions that one of his samples was treated with sodium; thinking that this might be the cause of the difference, a solution of sodium alcoholate in alcohol was prepared and examined (no. 6). This gives the bands found by Coblentz with the addition of one at 5.9 due probably either to the fact that more sodium was present or to the fact that a thinner film was examined (0.005

[1]Carn. Inst., p. 192.

mm. as compared to 0.01 and 0.18 mm.). Hence the specimen examined by Coblentz was probably a solution of sodium alcholate and not pure alcohol.

Homology in the Secondary Alcohols.—Curves have been obtained for three members of the secondary series: propyl (no. 11), butyl (no. 12) and capryl (no. 10); these are respectively the first, second and sixth members of the series. All have a characteristic band at about 7.7 which is not found in the primaries. The main bands noted in the primaries occur here, in the order propyl, butyl, capryl, as follows: 7.2, 7.3, 7.3; 9.0, 9.1, 9.1; 9.9, 9.8, 9.4. This again shows a shift toward the 9μ region as the series is ascended, the shift being less in the upper than in the lower members.

In this connection it is interesting to note that myricil alcohol, $C_{30}H_{61}OH$,[1] shows the characteristic bands of the primary alcohols: 3.0, 3.4, 6.9, 7.3, 9.4.

Homology in the Primary Acids.—I have added but one to the list of primary acids studied by Coblentz,[2] but while the data for this group of substances is largely from Coblentz, the point of view is somewhat different from his. Of the primary acids he has examined acetic CH_3COOH, valeric $CH_3(CH_2)_2CH_2COOH$, caproic $CH_3(CH_2)_5CH_2COOH$, stearic $C_{17}H_{35}COOH$, and cerotic $C_{26}H_{53}COOH$. In the present investigation butyric, $CH_3CH_2CH_2COOH$, has been added, so that there are at hand data on six members of the series, showing the following minima:

Acetic,	3.5	5.9	7.2	8.9	9.9	10.6	11.0	13.9
Butyric,	2.6	5.9	7.1	7.9	9.3	10.6	12.9	
Valeric,	3.6	5.9	7.1	7.9	9.1	10.7	12.2	13.3
Caproic,	3.5	5.9	7.0	8.0	9.1	10.8	11.6	12.5
Stearic,	3.5	5.9	7.0	7.8	9.2	10.6	12.2	13.3
Cerotic,	3.5	5.9	6.9	7.7		10.6	10.9	12.9

The first two bands are constant throughout the series, and the fourth and sixth show no particular shift, though the last one grows more prominent as the series is ascended. The third and fifth, however, shift towards the shorter wave-lengths as the series is ascended, the shift being larger in the lower members; the fifth grows weaker in the higher members, being absent entirely in cerotic acid. Beyond the sixth band there is no more regularitv. The

[1] Coblentz, Carn. Inst., p. 186.

[2] Carn. Inst., pp. 209–215.

spectra of the homologous acids, therefore, are very similar but wherever there is a shift, it is towards the shorter wave-lengths, and larger between the lower and simpler members of the series.

Homology in the Secondary Acids.—The transmission minima of the two secondary acids, isobutyric and isocaproic, have already been given (pp. 406–7). The characteristic bands of the secondary acids, as noted before, are the two near 8μ that take the place of the single one in the primaries. Both of these are shifted by 0.2μ to the shorter wave-lengths in the higher compound. Two other bands are also shifted: 7.1 to 7.0 and 9.2 to 9.1, so that whenever a shift occurs, it is toward the shorter wave-lengths as the compound becomes more complex.

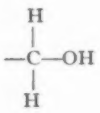
Homology in the Esters.—The complete series of esters as shown in the square array on page 403 could not be obtained on account of the cost of some of the necessary primary alcohols; isoalcohols, being cheaper, were in some cases used in place of the corresponding primary alcohols in the preparation of the esters, the result of course being an ester which differed from the normal ester in the same way that the iso alcohol differed from the normal alcohol. The comparison of primary and iso compounds has shown that their spectra are very similar, and a comparison of esters has shown that the spectra are very little affected even if CH_2 groups be shifted from the acid to the basic parts of the compound. Since the esters formed from the primary and iso alcohols differ only in the arrangement of the C and H in the basic part of the compound, it is probably safe to compare some of the primary and some of the iso esters as though they were all strictly homologous. Comparing the members of each column in the square array mentioned, the band in the 3.4 region shows a slight tendency to shift to longer wave-lengths as CH_2 is added to the compound. A small band lying between 4.8 and 5.0 is present in all the esters except in the column of ethyl compounds. On comparing the members of each row it is seen that a band is present at 6.9 or 7.0 in all the compounds except the acetates. The 4.3, 5.9 and 7.4 bands show no particular shift when comparing members of either rows or columns. That these same peculiarities exist far up the series is shown by methyl hexyl carbinol acetic ester (no. 24), which is, as its name indicates a

complex acetate. The 4.3, 5.9 and 7.4 bands are all in place and the region near 6.9 is still without any definite band.

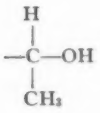
Successive members of a homologous series, therefore, show only slight changes in their spectra. In both the primary and secondary alcohols, in ascending the series, several bands are found to shift towards the 9μ region; in the primary and secondary acids a few bands are shifted toward shorter wave-lengths; in the esters the effect of homology is extremely slight, there being only a small shift of a single band near 3.4μ toward longer wave-lengths as the acid part of the compound is made more complex, and no shift at all as the basic part of the compound is made more complex

EFFECT OF CERTAIN GROUPS AND THEIR MODE OF LINKING.

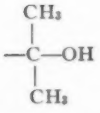
It is probable that the character of the groups present, the number of each kind, and their mode of linking all influence the absorption spectra. In discussing isomers several bands have been noticed to shift in such a way that it is most natural to attribute the shift to the change in the linking of the groups that compose the compound. For example the deepest band in the third absorption region of the alcohols was found to occur at 9.6 in all the primaries, at 9.1 in all the secondaries and at 8.6 in the one tertiary examined. These compounds differ in structure in that the hydroxyl group is linked to a carbon with successively one less hydrogen; that is, the primaries contain the group



the secondaries



and the tertiaries



It is evident that the above shift cannot be attributed to the mere presence of a CH_2 group in one case, of a CH in another and of a C

in the third, for these also occur in the iso alcohols where there is no such shift. Neither is the shift due to linking successively more CH_3 groups to the same C, for this also occurs in the iso alcohols. In these iso compounds, however, the C to which the additional CH_2 groups are linked does not carry the hydroxyl, while in the secondaries and tertiaries it does. Hence the shift must be attributed to the entire change in linking existing between the primary, secondary and tertiary compounds.

The secondary and tertiary linkings allow a greater freedom of vibration than the primary, as is shown by the new lines at 7.7 and 7.9 respectively. In the acids the same statement holds, for the change from primary to secondary manifests itself, as mentioned, by the appearance of two lines in place of one in the 8μ region.

It is probably safe to argue that those bands which coincide in the iso alcohols and the secondaries, but not in the primaries, are connected with the

$$\begin{array}{c} -CH- \\ | \\ CH_3 \end{array}$$

grouping. Such a band is that at 3.5 in the primaries and at 3.4 in the isomers. This indicates that the band near 3.5 is probably connected with the CH_3 group. The shifting of the 3.4 band in the homologous esters also indicates the probable connection between CH_3 and a band in this region.

A band such as that at 6.1 in the alcohols which dies out in the higher primaries, being absent entirely in butyl, but which persists longer in the isomers, shows that the same increase in molecular weight does not always have the same effect; the manner of loading the molecule is important.

The lines that are constant throughout an entire series are probably due to something which is constant in all the members; but in any one series several things are usually constant, so that from one series alone bands and groups cannot in general be correlated with certainty. However, by comparing these fixed bands in several series of related compounds, some fairly definite idea may be obtained as to the relation between particular groups and particular bands. With this in view, the alcohols, acids and esters will be compared.

The alcohols all have a strong band at 3μ and all above ethyl also have one at 3.5. This behavior indicates the possibility of a relation between the 3μ band and the OH group since both are present in all the alcohols. The 3.5μ band is most naturally thought of in connection with CH_2 or CH_3, for when there are many of these present, the band is deep and distinct while when there are only a few, as in methyl and ethyl and allyl (no. 9), the band does not appear. These suppositions are strengthened by the fact that the esters and the acids all have the 3.5 but not the 3.0 band. The esters of course have no hydroxyl and are rich in CH_2 so that the above suppositions hold without question, but the acids have an OH as part of the characteristic group acid, COOH, so that the above assumption must be restricted to apply only to an alcohol hydroxyl; this restriction is not arbitrary as the OH when linked to a CO has a different chemical behavior than when linked to a CH_2 or a CH.

The acids and esters have a strong band at about 5.9, a region in which the lower alcohols have a weak one, and the higher ones none at all. Aschkinass[1] ascribes this band in the alcohols to OH, but this is very unlikely in view of the fact that the band disappears in the higher members. By the present method of comparison it is natural to ascribe this band to something common to the acids and esters but not to the alcohols, that is, to the C = O group.

In the alcohols there is a band at 6.9, in the acids at 7.1, and in the esters a less pronounced one at 6.9 or 7.0 which is entirely lacking in the special case of the acetates. This may possibly be explained by assuming the 6.9 band in the alcohols due to OH, and the 7.1 band in the acids due to the COOH or the acid H only; the esters resulting from their combination would in that case not be expected to have a distinct band at that point.

A band appears in the esters at 7.4; since there are more CH_2 groups in the esters than in either the alcohols or the acids, this band is probably due to them. A band does appear at 7.3 in the higher alcohols, strengthening this view.

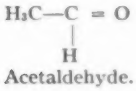
Another deep band at 8.0 in the acids and somewhere between 8.2 and 8.6 in the esters with no corresponding band in the alcohols will again tentatively be ascribed to C = O.

[1]Ann. d. Phys., 55, p. 431. 1895.

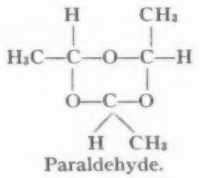
The bands at 9.5 in the alcohols, 9.2 to 9.8 in the esters, and 9.1 in the acids cannot be ascribed to any definite group, for they show no regularity even if each alcohol be compared with each acid and the corresponding ester.

Other facts are available to strengthen the above assumptions. Coblentz[1] gives curves for several hydrocarbons of the series C_nH_{2n+2}, all of which show bands at 3.4, 5.8, 6.9 and 7.3. The 3.4 and 7.3 bands practically coincide with those ascribed to CH_2 above. The 5.8 band is shallow in the hydrocarbons so that the CH_2 groups probably do not play much part in producing the deep bands found in the same place in the esters and acids, as already discussed above. The 6.9 band, however, is very deep, so that at first sight it seems natural to ascribe the deep bands in the alcohols at 6.9 and in the acids at 7.1 to CH_2; but the fact that this band is not characteristic of all the esters, as would be expected on account of the greater number of CH_2 groups, makes the other interpretation offered above seem more probable.

If the 3.0 and 6.9 bands are due to hydroxyl, those bands would not be expected in sodium alcoholate, and upon inspecting the curve (no. 6), they are not found. There is, to be sure, an indication that with greater dispersion a band might be found at 6.9, but this is only to be expected as the spectrum taken was that of a solution of sodium alcoholate in alcohol.



Acetaldehyde.



Paraldehyde.

The bands at about 5.8 and 8.2 in the acids and esters, which were ascribed to C = O occur also in the same place in acetone $CH_3—CO—CH_3$, in methyl carbonate $CH_3—O—CO—O—CH_3$, and in benzaldehyde C_6H_5CHO.[2] In acetaldehyde, CH_3CHO (no. 36), the two bands occur at 6.0 and 8.0, but in paraldehyde[3] the 5.8 band is very weak and the other is absent entirely, as is to be

[1]Carn. Inst., pp. 216–223.

[2]Coblentz, pp. 200, 201, 260.

[3]Coblentz, p. 261.

expected since the C = O group is not present, as shown by the formula. In all compounds, therefore, whose spectra are at hand, and which contain a C = O group, two bands occur near 5.8 and 8.2.

The spectra of acetaldehyde and paraldehyde show incidentally that the relative proportions of each kind of atom plays a secondary rôle as compared with the way in which the atoms are put together; the molecule of paraldehyde consists of three molecules of acetaldehyde, but the arrangement of the atoms is of course changed on polymerization; the spectra differ because the structure does.

To sum up:

OH has bands in the alcohols at 3.0 and 6.9.

CH_2 has bands in the alcohols, acids, and esters near 3.4.

has bands in the esters and higher alcohols near 7.3.

C = O has bands near 5.9 and 8.2.

ADDITIONAL FACTS BEARING ON THE PRECEDING QUESTIONS.

In order to test some of the preceding conclusions, several polyatomic alcohols, *i. e.*, alcohols with more than one OH group, and some dibasic esters, *i. e.*, esters of acids with two COOH groups, were examined. In the diatomic alcohols or glycols (nos. 33 and 34), just as in the monatomic alcohols, there are three general absorption regions before 10μ. In the first region there is a deep band at 3.2 in place of the one formerly found at 3.0. The second region, from 7.0 to 8.5 has only one minimum common to both the glycols examined; it occurs at 7.2. The third region has one band near 9.6. Outside of these regions there is a deep band at 6.0 and a somewhat less pronounced one near 4.2. The triatomic alcohol, glycerin (no. 35), also has three general absorption regions and in addition the new bands at 4.3 and 6.0, the latter being deeper than in the glycols. The minimum in the first region falls at 3.3; the second has two minima at 7.3 and 8.2; the third has a minimum at 9.6. The band in the first region is probably due to OH; if so, the addition of more hydroxyl groups shifts the band to the longer wave-lengths, the first additional OH causing more of a shift than the second. The 6.9 band which was also ascribed to OH in the monatomic alcohols is not distinct here, though the broadness of the band in the second region indicates its presence. The deep

band in the 3.5 region in the higher monatomic alcohols does not show in the polyatomic alcohols, probably because of the small proportion of CH_2 in these compounds as compared to OH. The 7.3 band however does show and is again probably a CH_3 band. The spectra of the polyatomic alcohols therefore have the same general characteristics as the monatomic ones; none of the previous correlations between groups and bands are contradicted. The main features of the spectra are the shift of the band in the first absorption region and the appearance of two new bands at 4.2 and 6.0; the former is due to the addition of more hydroxyl; the latter have not been correlated to any particular group.

The spectra of the acid and normal dibasic esters are almost identical as is shown by ethyl oxalate (no. 37) and diethyl oxalate (no. 40), and by ethyl succinate (no. 39) and diethyl succinate (no. 41). The spectra of the homologs ethyl oxalate, ethyl malonate, and ethyl succinate (nos. 37, 38, 39), and of diethyl oxalate and diethyl succinate (nos. 40, 41), are also very similar, just as the spectra of the monobasic homologs studied above. Up to about 8.6 and beyond 11.6 the absorption lines are practically identical in position, but the two lines between 8.6 and 11.6 show a shift toward shorter wave-lengths as the series is ascended: in ethyl oxalate, malonate and succinate these bands occur respectively at 10.0, 9.8, 9.5 and at 11.0, 10.7, 10.4; in diethyl oxalate and diethyl succinate they are found at 10.0, 9.7 and at 10.9, 9.5; the shift is less in the normal than in the acid esters. Hence the homologous dibasic esters lead to the same general conclusion that has been reached for other homologs: increase in complexity due to homology causes a small shift of several bands.

These esters also substantiate the conclusions regarding the correlation of groups and bands. There is no alcoholic hydroxyl group; neither is there a band at 3μ nor a deep one near 6.9 The two bands near 3.4 and 7.4, which in the monobasic esters were ascribed to CH_2, occur here at 3.5 and 7.5. Two bands, one at 5.9 and the other between 8.2 and 8.6, both of which were ascribed to C = O, occur here at 5.9 and 8.6. The prominent lines found here at about 4.5 and 7.7 are new, but cannot be correlated with any particular group or structure by comparing esters only. The shift

of the two bands between 8.6 and 11.6 can be correlated with the separation of the two carboxyl groups, or rather with the separation of one carboxyl, COOH, and one substituted carboxyl, $COOCH_2CH_3$ for in the lowest member of the series, ethyl oxalate, the two groups are joined directly, while in the next member, ethyl malonate, they are separated by one CH_2 group, in the next member, ethyl succinate, by two CH_2 groups, and so on. In the diethyl esters, where both carboxyls have been changed to $COOCH_2CH_3$, the shift is in the same direction, but smaller, due probably to the fact that more CH_2 is already present. These compounds therefore have spectra similar to the corresponding monatomic compounds: homologs show a similar behavior in the two cases, and the correlations made between particular groups and bands hold in the complex as well as in the simpler substances.

It will be noticed that practically all of the interpretations have been made from the parts of the spectra lying below 10μ. In this region the spectra of chemically similar compounds are similar to that the conclusions reached usually depend on a whole class of substances. In the region beyond 10μ, the spectra differ more materially, as was pointed out by Coblentz; this is the region where the individual characteristics of a substance produce the most pronounced effects, but on account of the nature of the changes produced, no definite conclusion can be drawn, from this investigation at least, as to the relation between particular bands and chemical structure. If it were required to identify a chemical compound by means of its absorption spectrum, the part of the spectrum lyine below 10μ would be useful mainly in determining the class to which the substance belongs, while the part beyond 10μ would determing the individual substance.

SUMMARY.

An apparatus has been built for taking graphic records of infrared absorption spectra.

The substances examined were all freshly prepared or purified, and were so selected as to permit the discussion of the several problems enumerated below. In the discussion of these problems, which all relate to series of compounds, use has been made mainly of the part of the spectra lying below 10μ; the part beyond 10μ gives the individual characteristics of each substance.

1. *Effect of Isomerism.*—Sometimes the spectra of isomers are practically identical, *e. g.*, isomerism in the esters due to transferring CH_2 from the acid to the basic parts of the compound; these compounds are all fairly similar chemically. A greater change in structure causes a greater change in the spectra, *e. g.*, primary-iso isomerism in the alcohols (nos. 4 and 7, 5 and 8). A more pronounced change still, causes more or larger shifts and perhaps the appearance of one or more new bands, *e. g.*, primary-secondary isomerism in the alcohols and acids (nos. 3 and 11, 4 and 12, 14 and 19).

2. *Effect of Homology* —Many different groups of substances were examined for homology: primary alcohols, secondary alcohols, primary acids, secondary acids, monobasic esters, and dibasic esters. In each of these series the spectra are similar; the addition of CH_2 usually causes small shifts of one or more bands, the shifts being larger in the lower members of the series, where the number of CH_2 groups already present is small.

3. *Effect of Certain Groups.*—The following groups and bands have been shown to be related:

OH, 3.0 and 6.9 in the alcohols.

CH_2, 3.4 in the alcohols, acids and esters.

CH_2, 7.3 in the esters and higher alcohols. (The band at 7.1 in the acids may be a CH_2 band also, but is probably a COOH band.)

C = O, 5.9 and 8.2 in all substances for which there are data.

4. *Effect of Mode of Linking.*—The 9.6 band in the primary alcohols shifts by 0.5μ to the shorter wave-lengths when the linking of the hydroxyl is changed to secondary, and by 0.5 more when changed to tertiary. (CH_2OH, CHOH, COH.)

The change from the primary to the secondary linking of the carboxyl group (CH_2COOH to CHCOOH), causes the doubling of a band in the 8μ region; this is true for both acids and esters.

The successive introduction of CH_2 groups between the two carboxyl (or methylated carboxyl) groups in the dibasic esters causes two bands lying between 8.6 and 11.6μ to shift toward shorter wave-lengths.

The C = O group is independent of its mode of linking to the

other parts of a molecule, for its bands occur at the same place in all substances for which there are data.

5. *Effect of the Number of One Kind of Group.*—As the number of CH_2 groups is increased, some bands remain unchanged and others shift slightly, as mentioned under effect of homology.

As the number of OH groups is increased in the alcohols, the 3μ band shifts toward longer wave-lengths.

6. *Effect of Polymerism.*—If two polymers differ greatly in structure, their spectra are also greatly different; *e. g.*, acetaldehyde and paraldehyde.

All these results agree with the conclusions of Abney and Festing, and of Coblentz, that the spectra of chemically similar compounds are similar.

The preceding generalizations are based on data covering really only a very small part of the entire chemical field, and are therefore decidedly subject to revision. They are stated in this rather decisive way for the sake of clearness only.

In conclusion, I wish to express my sincere thanks to Professors Kahlenberg and Koelker for their advice on the chemical part of the work, to Professor Snow for placing at my disposal all the necessary apparatus, and especially to Professor Mendenhall who not only suggested the subject but also greatly facilitated the work while in progress by his constant interest and helpful advice.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
August, 1908.

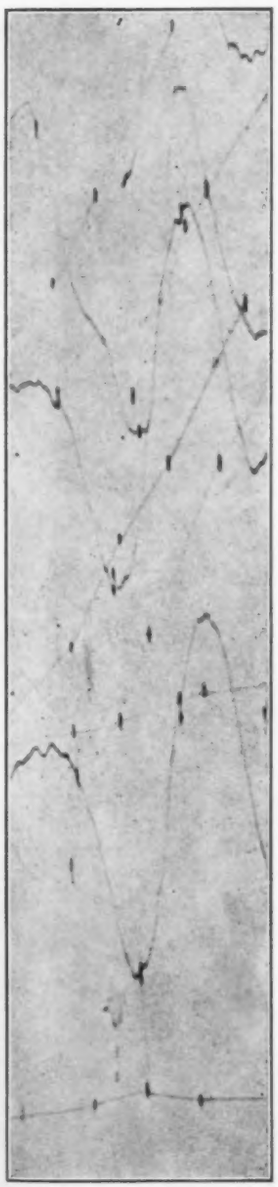
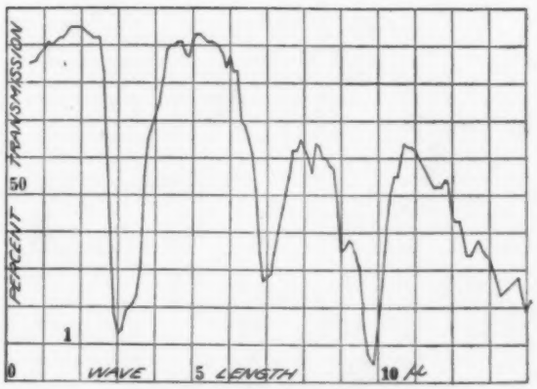
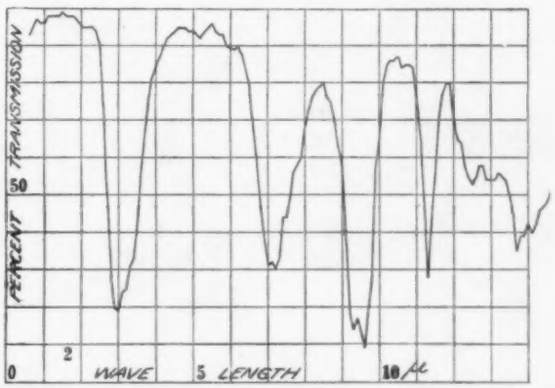


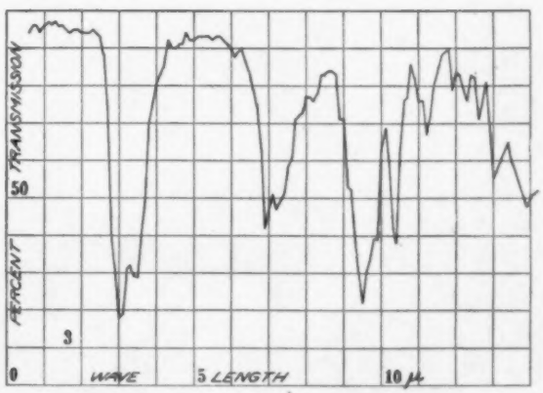
Fig. 3



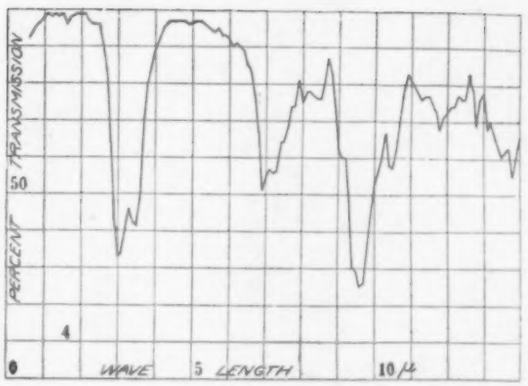
Curve 1. Methyl alcohol.



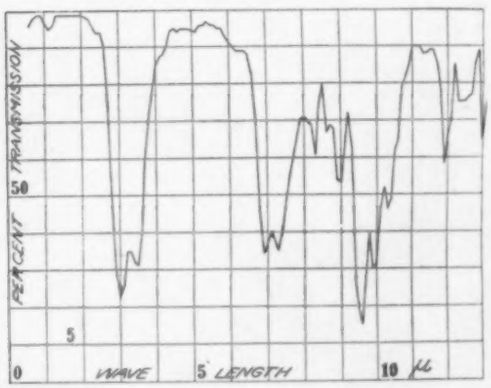
Curve 2. Ethyl alcohol.



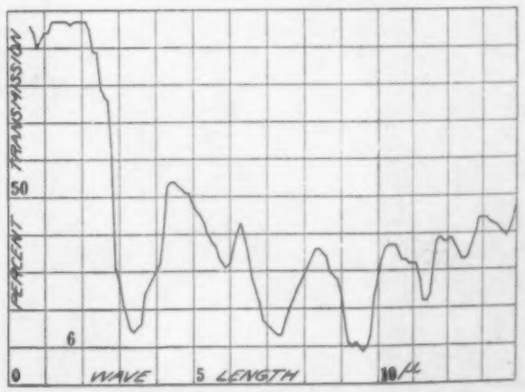
Curve 3. Propyl alcohol.



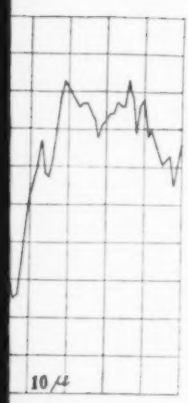
Curve 4. Butyl alcohol.



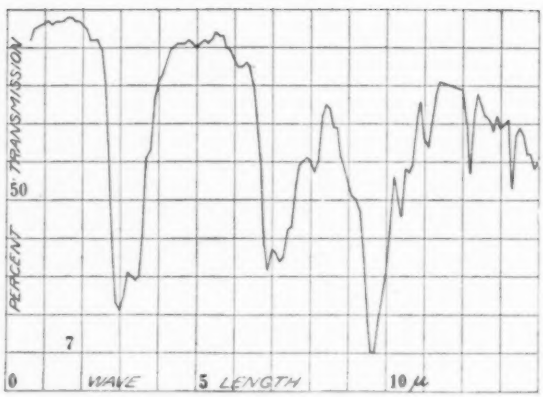
Curve 5. Amyl alcohol.



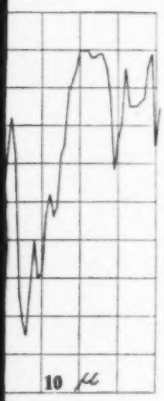
Curve 6. Sodium alcoholate.



ol.



Curve 7. Isobutyl alcohol.



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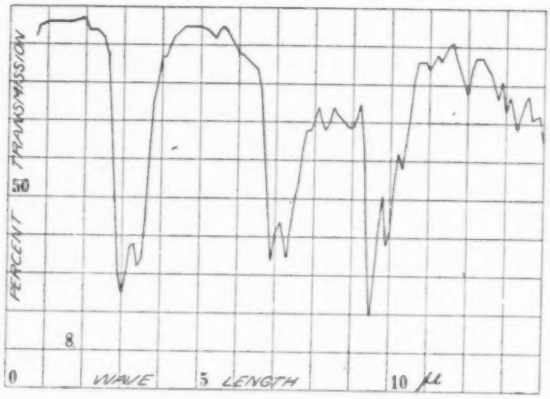
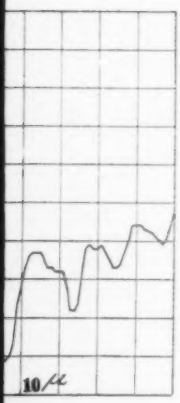


Curve 8. Isoamyl alcohol.



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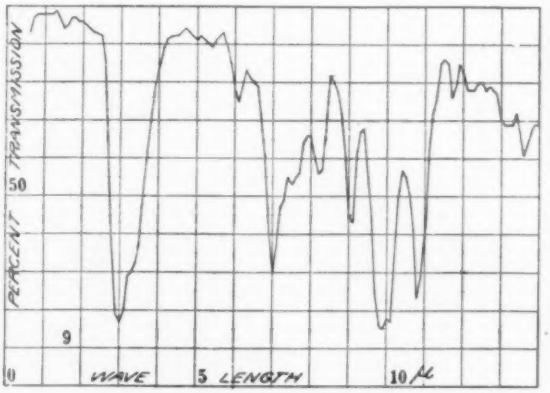

Curve 9. Allyl alcohol.

WENIGER: Infra-red Absorption Spectra. PLATE I.

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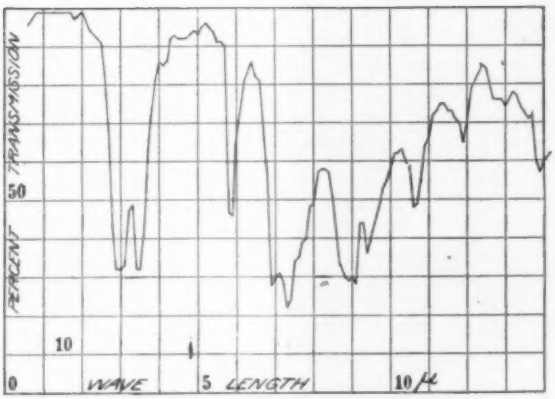
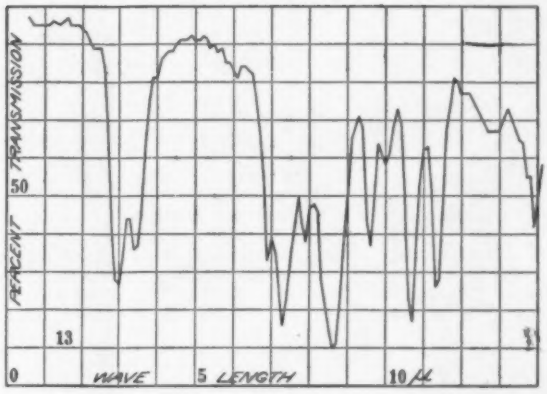
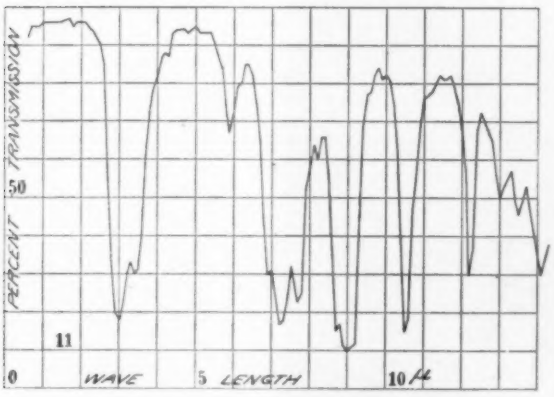


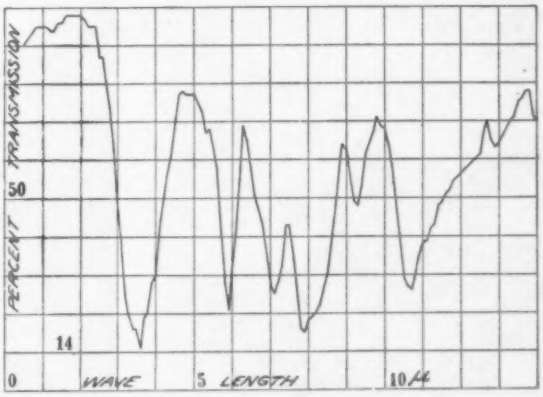
Curve 10. Capril alcohol.



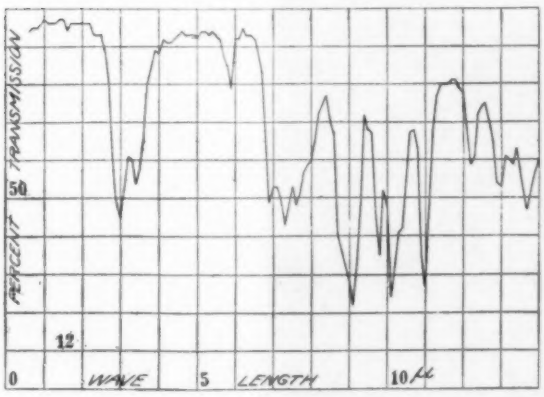
Curve 13. Tertiary amyl alcohol.



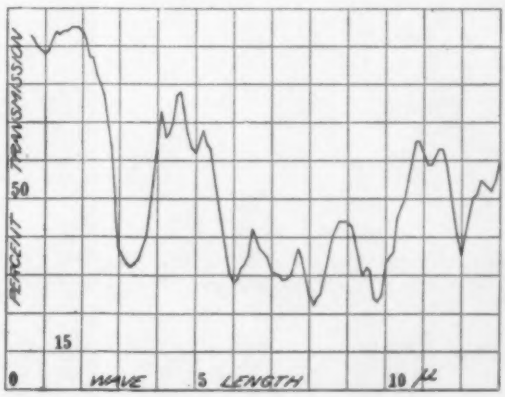
Curve 11. Secondary propyl alcohol.



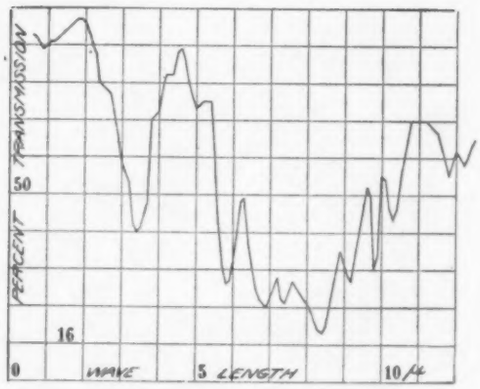
Curve 14. Butyric acid.



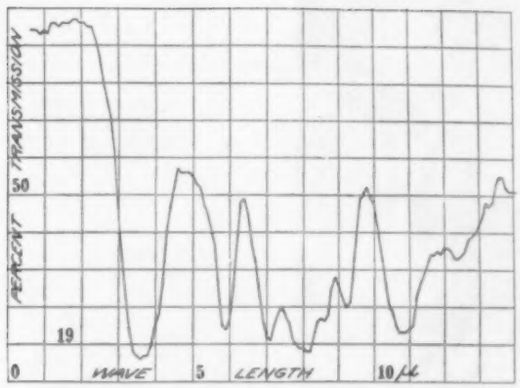
Curve 12. Secondary butyl alcohol.



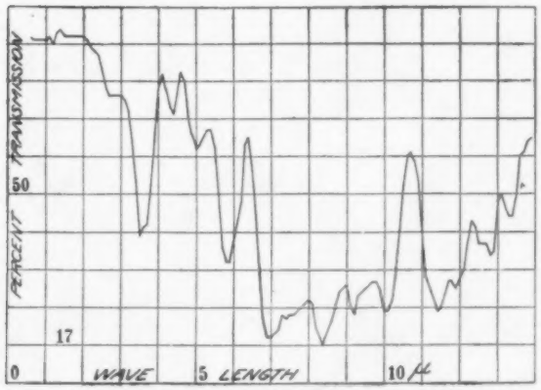
Curve 15. Methyl acetate.



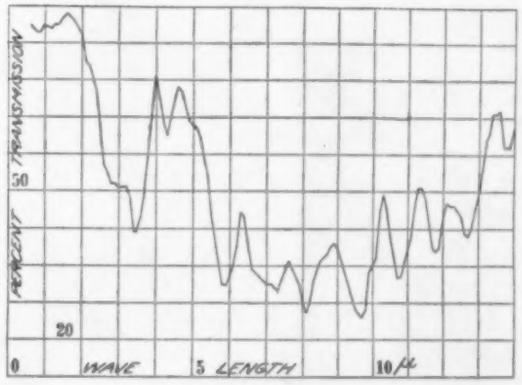
Curve 16. Methyl propionate.



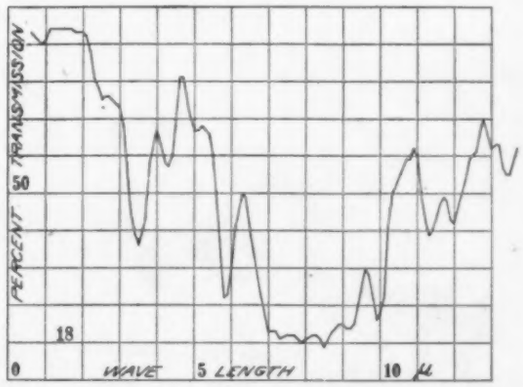
Curve 19. Isobutyric acid.



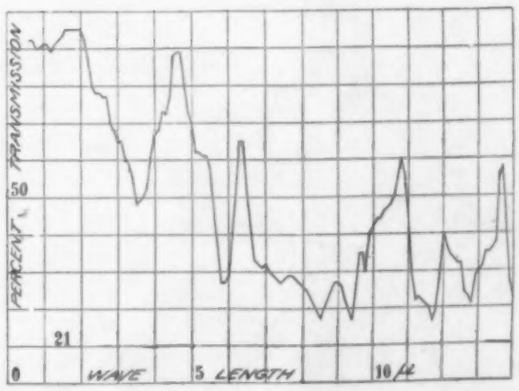
Curve 17. Methyl butyrate.



Curve 20. Ethyl acetate.



Curve 18. Methyl isovalerianate.



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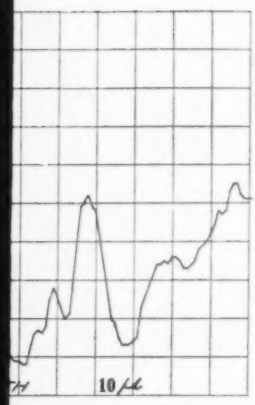

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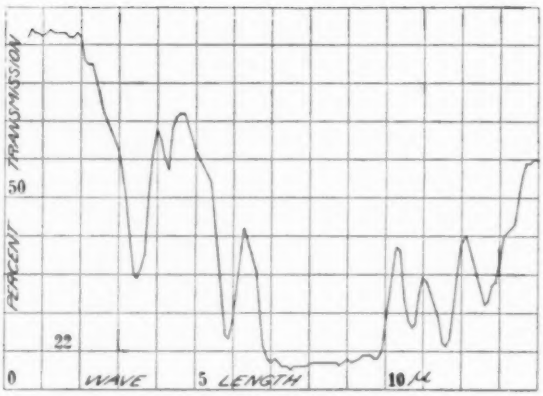
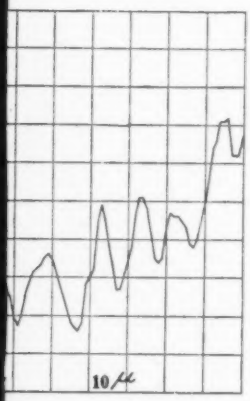


Curve 22. Ethyl butyrate.



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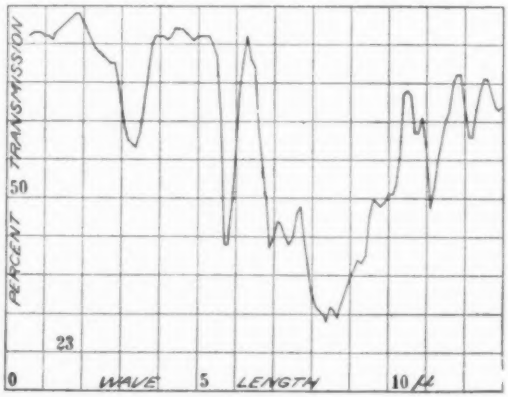
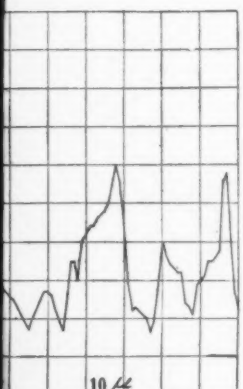


Curve 23. Methyl isobutyrate.



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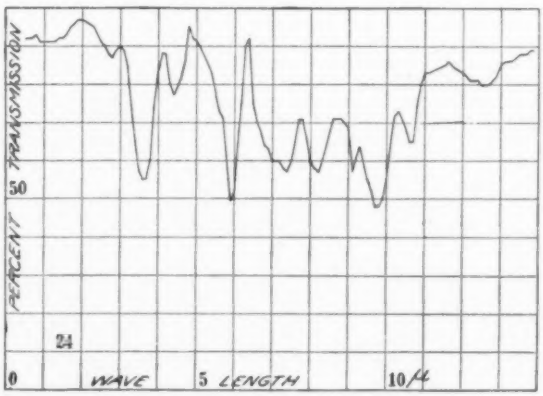

Curve 24. Methyl hexyl carbinol acetic ester.

WENIGER: Infra-red Absorption Spectra. PLATE II.

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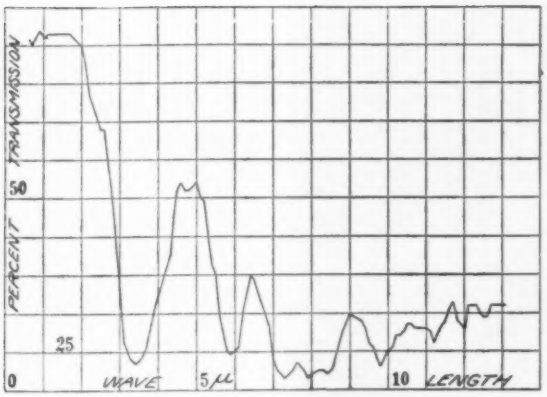
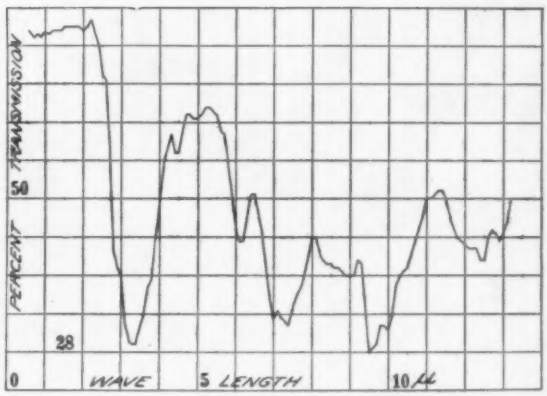
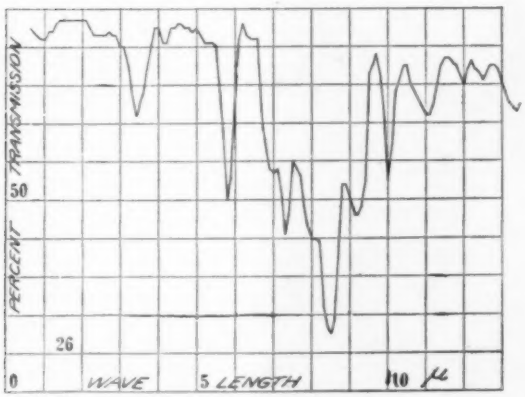


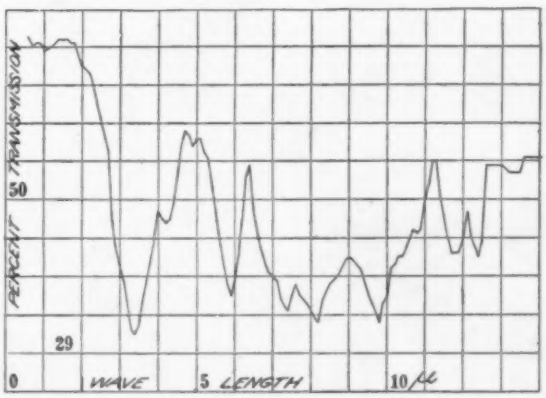
Curve 25. Isobutyl acetate.



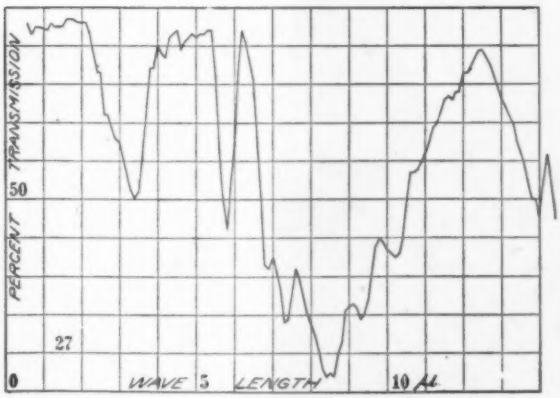
Curve 28. Isoamyl formate.



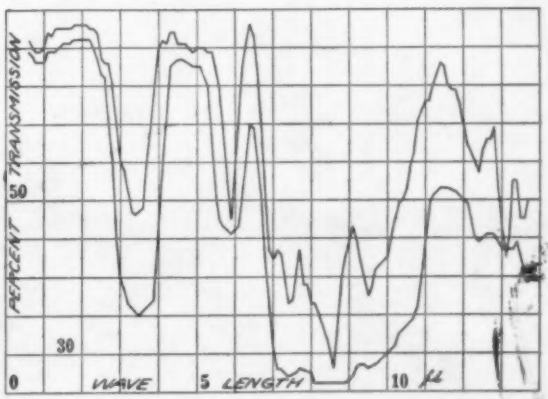
Curve 26. Butyl butyrate.



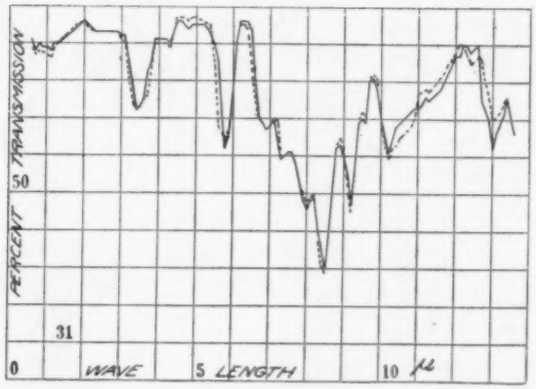
Curve 29. Isoamyl acetate.



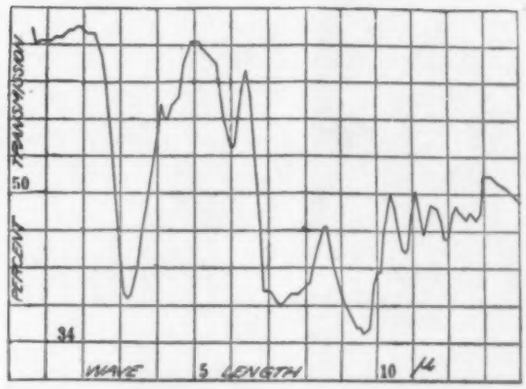
Curve 27. Isoamyl isobutyrate.



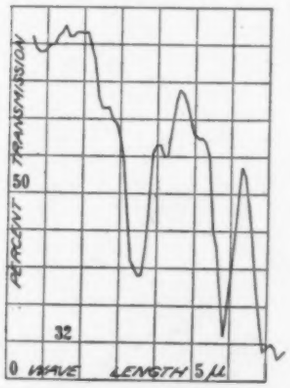
Curve 30. Isoamyl propionate.



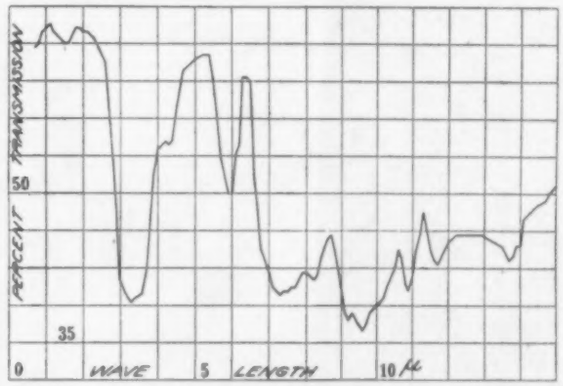
Curve 31. Isoamyl butyrate.



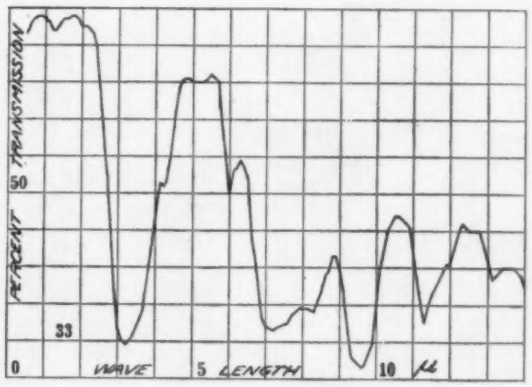
Curve 34. Propylene glycol.



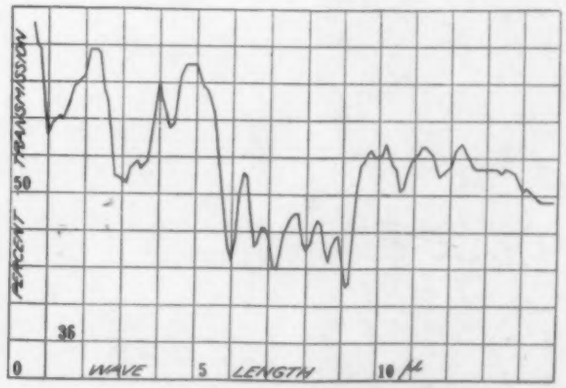
Curve 32. Isoamyl isovalerianate.



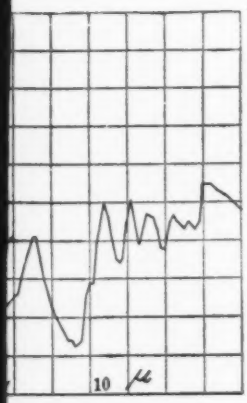
Curve 35. Glycerin.



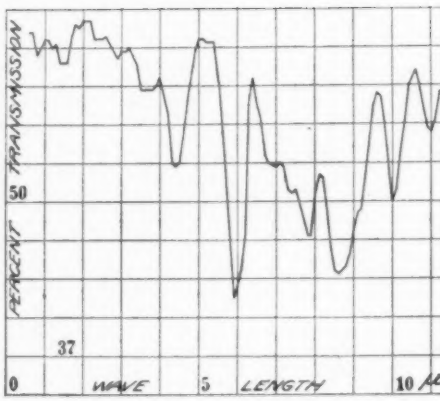
Curve 33. Ethylene glycol.



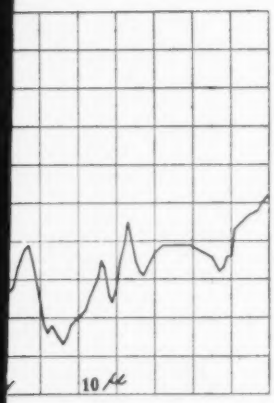
Curve 36. Acetaldehyde.



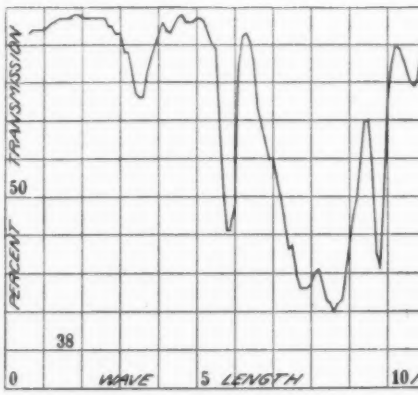
lene glycol.



Curve 37. Ethyl oxalate.



Glycerin.



Curve 38. Ethyl malonate.

taldehyde.

WENIGER: Infra-red Absorption Spectra. PLATE III.

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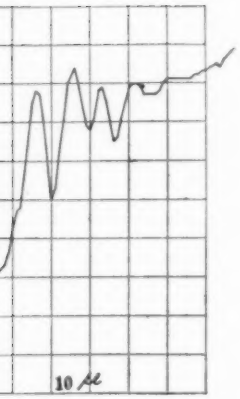
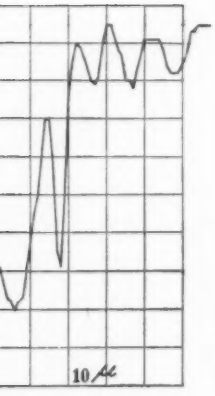
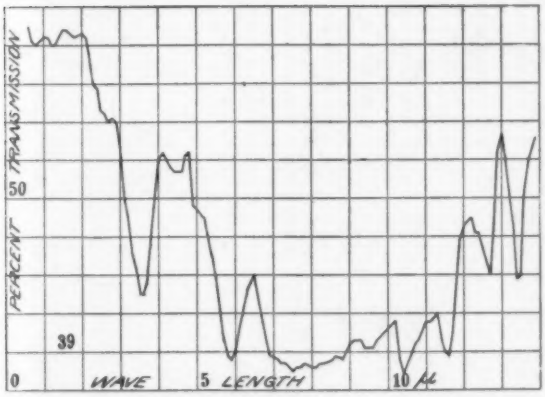


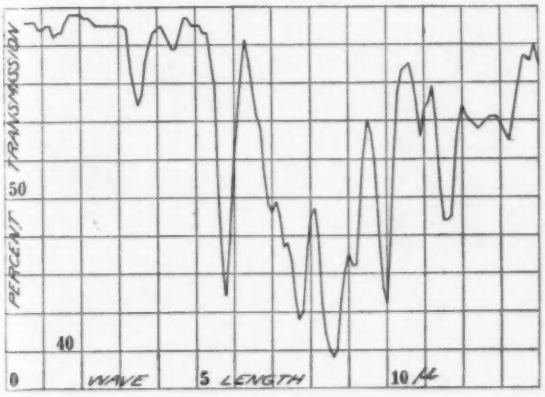
oxalate.



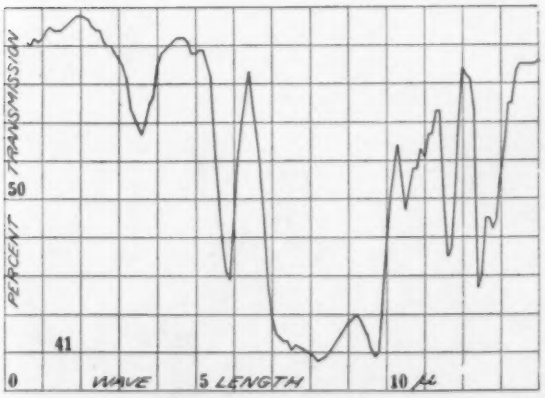
alonate.



Curve 39. Ethyl succinate.



Curve 40. Diethyl oxalate.



Curve 41. Diethyl succinate.

A STUDY OF SOME OF THE ELASTIC PROPERTIES OF A PLATINUM-IRIDIUM WIRE.

By L. P. Sieg.

I. Introductory.

THE remarkable elastic properties of a certain platinum-iridium wire containing 40 per cent. of iridium were first announced by Guthe.[1] In his experiments the wire was used as the suspension of a torsion pendulum. Although the amplitudes of vibration were less than 50 degrees, a marked increase both in the period and in the logarithmic decrement accompanied the increase in amplitude. Cylinders of equal mass but of different moments of inertia were suspended from the wire, set in vibration, and timed, but as a result of these experiments no change was observed in the logarithmic decrement-amplitude curves. This absence of any effect led to the supposition that the damping was proportional to the amplitude, and independent of the velocity.

The study of the elastic properties of such wires was continued by Guthe and the writer[2] during the latter part of 1908 and the early part of 1909. In that work, wires containing different percentages of iridium were used. The apparatus was so constructed that much larger amplitudes could be obtained than were obtainable before. As a result of the use of the larger amplitudes, additional information concerning the relation of period and of logarithmic decrement to the amplitude was obtained. It was found that although both the period and the logarithmic decrement varied directly with the amplitude for small values of the amplitude, they did not continue to do so for larger values of the amplitude. The periods at these large amplitudes tended to become constant, and at the same time the logarithmic decrements reached a maximum,

[1] K. E. Guthe, Proc. Iowa Acad. Sci., 15, p. 147, 1908; Abs. in Phys. Rev., 26, p. 201, 1908.

[2] K. E. Guthe and L. P. Sieg, Phys. Rev., 30, p. 610, 1910.

and then diminished. The peculiarities in the elastic behavior of these wires were found to increase as the percentage of iridium was increased. It was found that when the wires were tested by a static method they followed Hooke's[1] law, and that the torsional moment calculated from this static experiment was larger than the largest torsional moment found by the kinetic method.

In the present paper, the observations have been confined to the 40 per cent. platinum-iridium wire used by Guthe in his first experiments. It developed during the preparations of the second paper[2] that if any further experiments with the wire were to have value, a method of getting a definite period-amplitude relation must be found. The search for the determination of such a method has been the principal problem attacked in the present work, although several other points of interest have been developed. The writer believes that the value of these experiments, aside from their own interest, will be to suggest problems connected with ordinary wires, and methods of attacking these problems.

II. Apparatus and Method of Timing.

The apparatus was the same as that described in the former paper,[2] with the complete circular scale which was used in the last set of experiments therein described. The amplitudes of the vibrations were read by focusing the image of a wire, illuminated by an arc light, on the circular scale graduated directly in double degrees. The diameter of the scale used was 149.2 cm., thus giving a space of 2.6 cm. to a degree, and so enabling one to read with accuracy to tenths and to estimate in the smaller amplitudes to one one-hundredth of a degree. The double mirror was the same one used in the previous experiments.[2] It was possible, by the use of the complete circle for a scale and the double mirror, to read all the amplitudes with the exception of a very few when the mirror was end on. This equipment was a decided improvement over that used in the preceding experiments, for in those some of the important amplitudes were obtained only by interpolation. In all cases where

[1]Historically speaking, this is not Hooke's Law, but an extension of it discovered experimentally by Coulomb. Cf. Kelvin, Phys. Papers, Vol. III., p. 54.

[2]Guthe and Sieg, *loc. cit.*

the word "amplitude" is used, the word refers to what is ordinarily thought of as double the amplitude in angular harmonic motion, *i. e.*, the angular displacement from one extremity of the vibration to the other. In the few cases where the term is used in its strict sense, the phrase "amplitude from the center" is employed. The method of fastening the wire to the supports, and of attaching the various moments of inertia was the same as that described in the former paper. To the upper rod holding the wire was attached a torsion head, graduated into degrees, and having adjustable stops. This device made it possible to set the wire into vibration, and to hold it at practically constant amplitude. The method of timing was, with only one or two changes, essentially the same as that explained in the former paper. In all cases, unless otherwise stated, the periods are in reality half-periods. One important change, which in the light of some recently performed experiments proved of considerable value, was to tap the key at the end of the swing instead of at the middle. As this is contrary to usual procedure, it needs perhaps some justification. Briefly, if the amplitudes were measured at the ends of the swings and the periods were measured at the center, it would be necessary to plat the amplitudes and to obtain the amplitudes corresponding to the different periods by interpolation. While this refinement would not be necessary in an ordinary wire, it was in this case a decided necessity. However, the timing at the ends of the swings made it unnecessary to plat the amplitudes in order to get corrected values, for in each case tried the points observed fell on a smooth curve. Of course at the end of each experiment, when the amplitudes were down to about forty degrees, it was necessary to transfer observations to the center. yet as this resulted in a break of only a quarter period this error was of vanishingly small significance. From this point down the periods were taken in one of two ways: either by the method of coincidences or by the method of middle elongations. To average twenty readings on the tapes was found to give practically as smooth a curve as to average forty readings and the curve so obtained more closely agreed with the facts. To make perfectly clear how the periods were obtained, the method will be briefly described. A drum geared to a motor running at nearly constant speed wound

the tape from the roll, drawing it under a pen attached to the armature of an electromagnet. A Bond and Son's siderial, break-circuit chronometer in circuit with the electromagnet gave double-second marks on the tape. Connected with the recorder by a separate circuit was a tap key, which was closed, as explained above, at the ends of the vibrations. In this way there was recorded on the same tape the times at which these positions were reached and the double-seconds. When the amplitude had decreased to a value of from 15 to 20 degrees, the tape was abandoned, and the periods thereafter were obtained as explained above. Upon the tape record, the chronometer times of these turning points were recorded in hours, minutes, seconds, and hundredths of a second. Supposing that t is this recorded time for the fifth vibration, and that t' is the time for the twenty-fifth vibration, then $t' - t$ is the time elapsed between these two vibrations. This difference divided by 20 is used as the period of vibration of the mean swing; in this case, the fifteenth. In this way the errors arising from individual observations are diminished; and while this method is not an exact one, numerous tests have shown that it gives essentially correct values. A sample of one of the curves connecting period and vibration number given in Fig. 1. The figure shows how well the observed values fit a smooth curve, and how in most cases it was unnecessary to correct the period readings.

III. Relation between Amplitude and Period.

In the former experiments it became quite evident that the variation of period of vibration with the amplitude was, except under very special circumstances, not a definite thing. It seemed highly necessary, therefore, to determine if possible some definite treatment of the wire which for any initial amplitude would lead to a fixed relation between the subsequent amplitudes and periods. The necessity of determining some definite method of treatment is shown by the widely different relations existing between these two quantities, when they are observed under different circumstances. In the former experiments, with the exception of a few observations taken at the end of the work, this peculiar variation of amplitude and period was overlooked on account of the fact that preceding

any set of observations the wire was nearly always annealed, and was always twisted through a large amplitude. The following experiments seem at first sight to indicate that the elastic behavior of the wire is of an extremely unconstant and variable nature, but this conclusion is contradicted by the more usual behavior of the wire under static conditions.

1. *Increasing Initial Amplitudes.*—In the first place a set of experiments was carried out, showing the variation of the period-ampli-

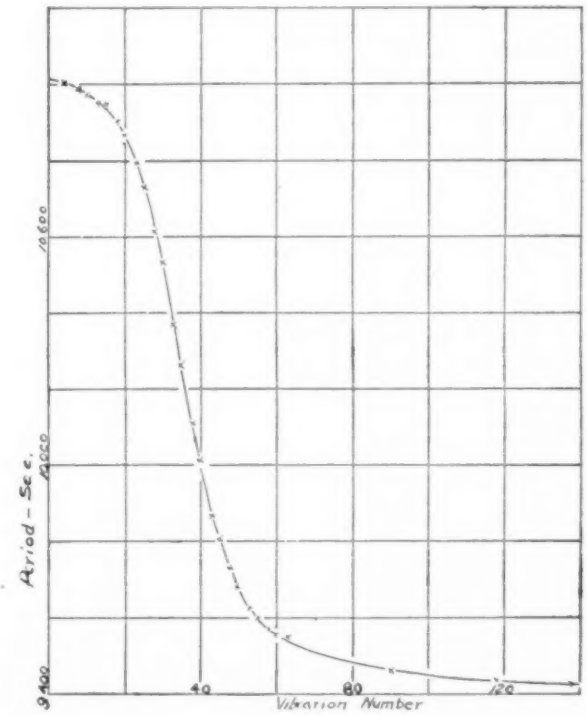


Fig. 1.

tude curve with different initial amplitudes. The wire was annealed at dull red heat by a current of 2.5 amperes, for about 30 seconds. Care was taken not to allow the wire to vibrate through more than fifteen or twenty degrees after this treatment. The wire was then carefully twisted through a certain small amplitude and timed by the method described above. After a rest of a day the wire was

twisted through a larger amplitude and timed as before. This was continued with constantly larger initial amplitudes until at the sixth observation the amplitude had reached a value of 788 degrees. This was an amplitude from the zero position of 394 degrees, and a twist per centimeter of length of 9.8 degrees. The results of this set of experiments are given in Table I., and graphically shown in

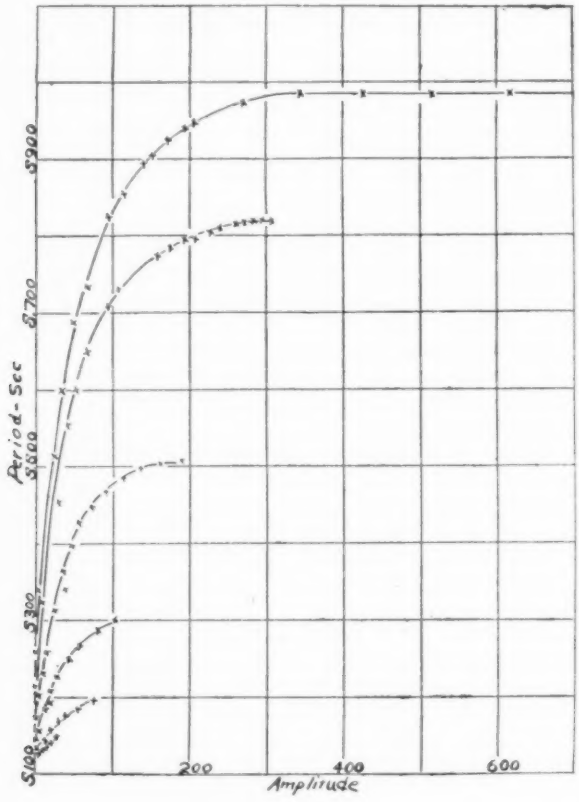


Fig. 2.

Fig. 2. This particular experiment was recorded in the former paper, but as the experiment had been rather hastily done, it was for the sake of certainty repeated here.

It will be seen that for small initial amplitudes the wire is in its behavior not far different from ordinary wires, *i. e.*, its change in period with amplitude is small, but it will be seen also that as the

TABLE I.

Length 40.2 *cm. Moment of Inertia* 980 *g. cm*^{2}.

November 30.			December 1.			December 2.		
No.	Amp.	Period.	No.	Amp.	Period.	No.	Amp.	Period.
0	28.1	5.149	0	74.5	5.198	0	102.0	5.300
10	26.6	.147	15	62.2	.192	10	83.0	.287
20	25.1	.145	25	55.0	.186	30	52.8	.262
30	23.6	.144	35	49.0	.183	40	42.6	.250
40	22.4	.142	50	41.3	.178	50	34.2	.238
50	21.2	.141	70	33.3	.171	60	28.3	.228
70	19.2	.139	90	27.3	.165	70	23.8	.218
90	17.4	.138	120	21.3	.158	80	19.8	.208
110	16.2	.136	150	17.0	.153	90	16.8	.200
130	15.0	.135	180	13.5	.149	110	12.1	.188
150	14.0	.135	200	12.0	.147	130	10.0	.180
170	13.2	.134	210	11.3	.145	140	8.9	.175
190	12.4	.133	230	10.3	.143	160	7.3	.167
210	11.8	.133	240	9.8	.143	180	6.2	.161
230	——	.132	250	9.4	.142	200	5.3	.157
300	9.2	.131	300	7.6	.140	230	4.4	.155
350	8.2	.130	350	6.3	.138	250	3.9	.154
400	7.4	.129	400	5.4	.135	350	2.6	.150
450	6.9	.129	450	4.7	.133	400	2.3	.148
973	3.31	.128	874	2.35	.133	450	2.1	.147
December 3.			December 4.			December 5.		
No.	Amp.	Period.	No.	Amp.	Period.	No.	Amp.	Period.
0	190.0	5.508	0	308	5.820	0	738	5.986
10	135.0	.498	5	249	.813	5	619	.986
20	91.0	.468	10	195	.795	10	517	.986
30	58.2	.427	15	150	.771	15	426	.986
40	36.3	.364	20	109	.730	20	344	.985
50	24.8	.312	25	78.0	.676	25	270	.972
60	17.3	.274	30	53.0	.601	30	206	.946
70	13.3	.249	35	37.0	.520	35	150	.905
90	8.6	.226	40	27.0	.435	40	104	.847
110	6.0	.213	45	20.0	.390	50	46	.673
130	4.6	.201	50	16.0	.365	60	22	.515
150	3.7	.193	60	10.0	.326	65	17	.465
160	3.4	.191	70	7.0	.300	70	13	.425
170	3.1	.189	80	6.0	.271	80	9	.383
180	2.8	.187	90	4.8	.250	90	6.1	.362
200	2.5	.184	100	4.1	.234	100	5.0	.340
220	2.2	.182	120	3.08	.227	120	3.7	.300
240	2.1	.180	140	2.4	.222	140	2.75	.280
250	2.0	.178	160	2.09	.216	160	2.1	.265
300	1.6	.172	170	1.98	.214	210	1.4	.259

initial amplitude increases, the periods corresponding to a given amplitude increase in a remarkable manner. Not only does the period increase, but so also does the internal friction, as is evident when we examine the total number of vibrations necessary to bring the wire down to a certain small amplitude, say five degrees.[1] This number will be noted in Table II.

TABLE II.

Date.	$\theta°$	Vibrations to 5°.	t	θ^2	θ^2-25	$\frac{\theta^2-25}{t}\times 10^2$
Nov. 30	14.1	625	3,270	199	174	5
Dec. 1	37.3	425	2,190	1,391	1,366	62
" 2	51.0	210	1,093	2,601	2,576	236
" 3	95.0	125	664	9,025	9,000	1,355
" 4	154	88	484	23,716	23,691	4,895
" 5	369	100	567	136,161	136,136	24,010

In the column headed $\theta°$ is the first obtained reading for the maximum amplitude from the rest point. In column headed t is the number of seconds which elapsed while the pendulum fell from $\theta°$ to 5°. The numbers in column $\theta^2 - 25$ give a measure of the loss in energy during this time, and the numbers in the last column give the relative values for the rate of dissipation of this energy. Relative values can be obtained by representing the loss in energy in falling from a twist $\theta°$ to, say, an angle of 5°, by the expression $C(\theta^2 - 5^2)$, where C is a constant, and by dividing this by the number of seconds required for the wire to come down to five degrees. If it were desirable the actual energy dissipation in ergs per second might be determined from the knowledge of the torsional moment of the wire. However as the torsional moment requires for its determination a knowledge of n, the coefficient of simple rigidity, and as n will be shown later to have different values, depending on whether it is measured by the kinetic or by the static method, the exact determination of the torsional moment is perhaps a difficult

[1]Kelvin [Math. and Phys. Papers, Vol. III., p. 25] observed in the case of an aluminum wire that the vibration "subsided much more rapidly from amplitude 20 to amplitude 10, when the initial amplitude was 40, than when it was 20." In the former case the number of vibrations from 20 to 10 was 96, and in the latter case the number from 20 to 10 was 112.

matter, and would largely rest on the definition for n. Still further it must be admitted that, in this calculation, it has been assumed that the torque possessed at the angle θ in the actual experiment is the same as the static torque for the same angle θ. So with this assumption, the relative values for the rate of energy loss are calculated. It is of course evident that this method gives only the average values. Somewhat similar values would be found for ordinary wires, and these values are of chief interest when compared with the values obtained under different circumstances with the same wire (cf. Table V*b*). It will be noticed, under the column "vibrations to 5°," that down to a certain point the number decreases notwithstanding the fact that the amplitude continually increases, but that at a certain point the number of vibrations commences to increase. This is comprehensible when we examine the period-amplitude curve for the largest initial amplitude and note that after a certain amplitude has been reached, the period approaches saturation, as it were. That is to say, after a certain starting amplitude has been reached, the further increases in amplitude tend to give period-amplitude curves that more nearly approach each other when traversing common ground; and whatever it is that has caused this enormous increase in internal friction, has apparently reached such a state that no large changes are possible. So from this point on, we should expect that for larger amplitudes more vibrations would be necessary to bring the amplitude down to 5°. This point is also evident from similar reasoning, when we examine the curves and values for the logarithmic decrement. These latter have been calculated for this set of experiments, and although the logarithmic decrement here loses its original significance, it is still very instructive in the information it gives as to the damping. The following values for the decrement (Tables III. and IV.) were calculated from another set of observations, similar to these in every respect, except that the wire was annealed between each two experiments. The final results in the two cases are practically identical. To save space only one complete table is given, and for the other six experiments, are recorded merely the finally calculated decrements and the corresponding amplitudes. In all cases common logarithims are used. Owing to the large initial

decrease in the amplitudes, the decrement is taken over a very small range of amplitude, this range being gradually increased. To get the amplitude corresponding to a given value of the decrement, the value is taken from the original tables corresponding to the mean vibration number used in the interval. The results are graphically shown in Fig. 3, where curves are drawn corresponding to the gradually increasing initial amplitudes.

TABLE III.

Length 40.2 *cm.* *Moment of Inertia* 980 *g. cm*^{2}.

$m-n$	A_m	A_n	Log A_m	Log A_n	Log (A_m/A_n)	Log. Dec.	MeanAmp.
4	639	526	2.8055	2.7210	.0845	.0211	582
4	582	476	.7649	.6776	.0873	.0218	526
4	526	427	.7210	.6304	.0906	.0227	476
4	476	381	.6776	.5809	.0967	.0242	427
4	427	337	.6304	.5276	.1028	.0257	381
4	381	295	.5809	.4698	.1111	.0278	337
4	295	220	.4698	.3424	.1274	.0319	256
4	220	158	.3424	.1987	.1437	.0359	188
4	158	110	.1987	.0414	.1573	.0393	132
4	110	75	.0414	1.8751	.1663	.0416	90.7
4	75	53	1.8751	.7243	.1508	.0377	62.3
8	62.3	33.8	.7945	.5289	.2656	.0332	44.4
11	53.2	26.3	.7259	.4200	.3059	.0278	38.4
14	44.4	21.9	.6474	.3404	.3070	.0219	33.8
17	38.4	19.3	.5843	.2856	.2987	.0176	26.3
20	33.8	16.9	.5289	.2279	.3010	.0151	21.9
20	16.9	12.3	.2279	.0899	.1380	.0069	14.2
20	12.3	10.1	.0899	.0043	.0856	.0043	11.1
40	10.1	8.0	.0043	0.9031	.1012	.0025	9.0
145	8.0	4.54	0.9031	.6571	.2460	.0017	5.82
159	4.54	3.21	.6571	.5065	.1506	.0009	3.80

2. *Decreasing Initial Amplitudes.*—The next set of experiments was similar to that mentioned in the preceding section, except that the wire was started at large amplitude at the first, and then successively started at lower amplitudes. It was thought that this would settle the question as to whether the period depends merely upon the amplitude, or whether, in a more complicated fashion, it depends to a large extent upon the preceding history of the wire. The latter was found to be true, and the results for the amplitude-

TABLE IV.

Mean Amp.	Log. Dec.	Mean Amp.	Log. Dec.	Mean Amp.	Log. Dec.
18.2	.00072	46.1	.00208	59.3	.00403
17.8	98	43.8	218	54.1	393
17.4	100	41.7	219	49.4	386
17.0	102	39.7	208	45.4	354
16.6	105	37.7	219	41.9	342
16.3	80	35.9	205	39.0	313
16.0	81	33.8	216	36.3	287
15.7	84	32.6	213	34.0	268
15.3	85	31.1	195	28.5	233
15.0	86	27.8	195	24.0	198
14.7	88	23.4	176	20.3	165
13.3	80	20.4	212	13.0	109
11.5	66	18.1	150	6.72	060
7.95	72	14.4	174	3.88	044
6.08	53	10.7	119		
5.00	45	7.83	106		
4.26	50	5.57	088		
3.72	41				
3.27	41				
115	.00944	194	.0196	400	.0193
103	950	177	203	366	199
92.4	942	161	202	333	209
82.9	953	147	207	302	216
74.2	958	133	220	273	227
66.5	944	120	226	245	240
59.7	944	96.7	239	194	262
53.5	930	77.7	240	150	304
43.3	919	62.2	237	112	331
35.2	887	50.1	228	82	366
28.9	824	41.0	205	59.2	334
24.1	756	34.3	186	45.9	313
20.5	656	27.5	150	32.6	296
17.7	590	21.7	112	25.6	245
13.7	502	14.7	0646	21.0	186
11.2	386	12.4	0324	14.0	118
7.2	132	9.8	0387	9.45	069
5.33	095	7.6	0172	6.76	0458
3.64	119	6.2	0181	4.59	0262
		4.19	0081	3.31	0156

period relations are shown in Table V*a*, Fig. 4, and for the amplitude-logarithmic decrement relations in Table VI., Fig. 5. In Table V*b* is a calculation of the relative values for the rate of dissipation of

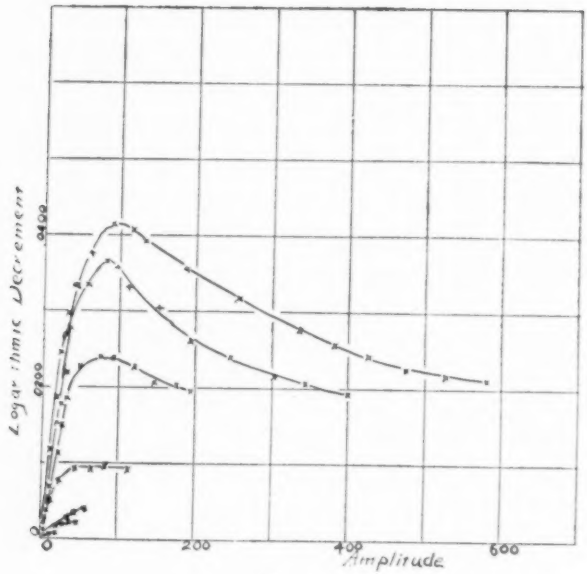

Logarithmic Decrement
0400
0300
0
200
400
600
Amplitude

Fig. 3.

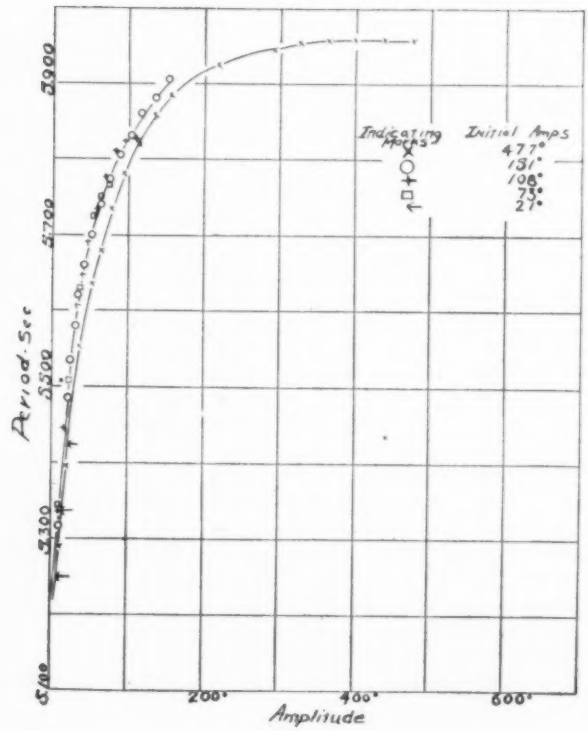

Period-Sec
3900
3700
3500
3300
3100
200
400
600
Amplitude
Indicating Marks
Initial Amps
477°
131°
106°
75°
27°

Fig. 4.

TABLE V (*a*).

Length 40.2 *cm.* *Moment of Inertia* 980 *g. cm*^{2}.

December 7.			December 9.			December 10.		
No.	Amp.	Period.	No.	Amp.	Period.	No.	Amp.	Period.
0	477	5.958	0	151	5.905	0	108	5.825
2	437	.958	4	117	.860	4	81	.810
4	398	.958	10	74	.773	10	48.3	.690
6	361	.957	16	43	.660	14	33.3	.604
8	326	.953	20	30	.580	16	27.9	.562
15	219	.925	24	21	.485	20	19.9	.485
24	113	.820	28	16.2	.415	26	13.3	.387
30	64	.678	35	11.4	.345	30	10.9	.350
34	43	.595	45	8.1	.297	36	8.7	.314
40	26	.475	55	6.4	.267	40	7.8	.297
55	13	.330	65	5.4	.253	50	6.1	.263
65	10	.290	75	5.0	.247	55	5.5	.253
80	7	.255	85	4.4	.244	60	5.1	.245
85	6.7	.248	95	4.0	.240	80	4.2	.240
100	5.7	.236	100	3.8	.239	100	3.4	.236
101	5.55	.236	121	3.23	.231	136	2.52	.231
179	3.06	.231	174	2.47	.225	190	2.01	.222
237	2.39	.227	232	2.02	.224	244	1.67	.222
301	1.92	.219	299	1.64	.222	303	1.41	.222
370	1.57	.216	371	1.38	.222	362	1.22	.222

December 11.			December 12.		
No.	Amp.	Period.	No.	Amp.	Period.
0	73.3	5.765	0	20.7	5.425
10	30.0	.580	6	14.0	.375
12	21.4	.509	10	11.4	.348
20	13.9	.403	14	9.6	.320
26	10.2	.342	16	8.9	.308
30	8.7	.315	20	7.8	.292
36	7.2	.289	24	6.9	.280
40	6.4	.277	26	6.6	.275
50	5.2	.256	30	6.1	.265
55	4.8	.250	35	5.4	.257
60	4.4	.245	40	5.0	.250
70	3.9	.241	45	4.6	.245
80	3.4	.239	50	4.3	.240
90	3.2	.236	60	3.8	.235
100	3.0	.235	70	3.4	.238
115	2.8	.232	80	3.2	.232
125	2.7	.230	90	3.0	.230
135	2.6	.228	100	2.8	.228
142	2.62	.225	157	2.01	.222
238	1.49	.222	220	1.66	.222

TABLE V (*b*).

Date.	θ°	Vibrations to 5°.	t	θ^2	θ^2-25	$\frac{\theta^2-25}{t}\times 10^2$
Dec. 7	239	114	620	57121	57096	9209
" 9	75.5	75	407	5700	5675	1394
" 10	54	63	335	2916	2891	863
" 11	36.7	52	286	1347	1322	462
" 12	10.4	40	212	108	83	39

energy (obtained as described in the preceding section), together with a column for the number of vibrations down to 5 degrees. A comparison of the two tables [Tables II. and V*b*] will clearly bring out the essential differences between these two sets of experiments.

Since the points in Fig. 4 lie so closely together, only through those of the two largest initial amplitudes are curves drawn. However the loci corresponding to the different initial amplitudes are indicated on Fig. 4, and the general relations of their paths can be

TABLE VI.

Dec. 7.		Dec. 9.		Dec. 10.		Dec. 11.		Dec. 12.	
Amp.	Log.Dec.	Amp.	Log.Dec.	Amp.	Log.Dec.	Amp.	Log.Dec.	Amp.	Log.Dec.
437	.0197	143	.0260	94	.0312	62.3	.0367	17.9	.0293
398	208	126	295	69	363	43.4	400	14.0	246
361	214	110	298	48.3	398	30.0	351	11.4	209
326	227	95	346	33.3	397	19.9	371	9.6	169
271	247	81	352	23.3	367	13.2	251	8.1	144
219	274	62	383	17.1	307	10.2	181	6.8	107
175	309	52	397	13.3	242	8.7	148	5.4	0836
133	350	43	430	10.0	175	7.4	136	4.6	0655
94	377	35	391	8.7	135	6.4	109	3.6	0428
78	417	21	335	7.1	110	5.0	0749	3.0	0290
43	394	16.2	241	6.1	0933	3.9	0560	2.4	0253
26	302	11.4	177	5.1	0540	3.1	0241	1.84	0132
19	222	8.1	125	2.52	0291	2.75	0158		
13	1505	6.4	0881	1.84	0149	2.6	0077		
10	1054	5.2	0494	1.54	0125	2.09	0026		
8	0870	4.7	0464	1.32	0106				
6.5	0589	3.8	0373						
6.1	0511	3.6	0357						
2.16	0149	2.9	0220						
1.75	0127	1.51	0104						

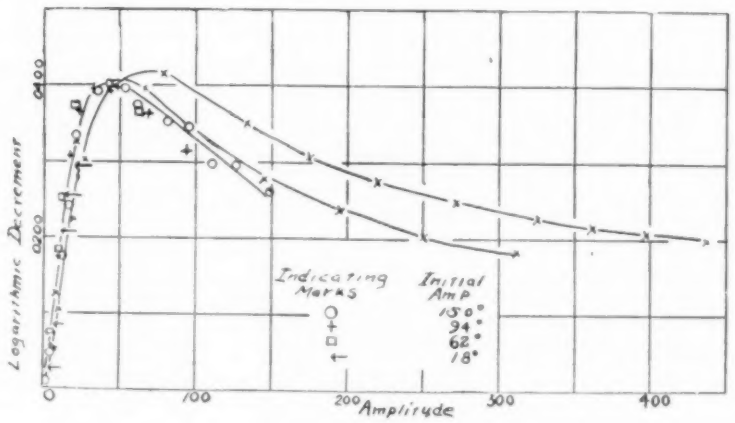


Fig. 5.

seen. It appears at first sight from this figure that in this case the wire had been put in a certain condition as a result of the first large distortion, and that this condition had remained in the wire. There seems to have been a slight tendency for the wire in the lowest starting amplitude to regain the original values it had in the experiments which were the reverse of this one. To satisfy myself concerning this point one last experiment was made which quite clearly brought out the tendency toward self-restoration in the wire. It seemed possible that in coming by *gradual* steps from the large amplitudes down to the smaller ones, the tendency for the wire to restore itself had been masked, and that a better procedure would have been to treat the wire as follows: first, anneal to red heat with a current of 2.5 amperes; second, vibrate through the maximum amplitude, 360 degrees from the center; allow to die down naturally without timing; and third, vibrate at a small amplitude, say 40 degrees, and time in the usual way. For the next experiment, repeat steps one and two, and then for the third step vibrate through about 70 degrees, and so on with larger amplitudes for this last step. These experiments were performed, and the results are shown in Table VII., Fig. 6. Curve (*a*) represents the period-amplitude relation in the lower values for the large original twist (second step above; in this one observation the step was timed), while curves (*b*), (*c*) and (*d*) represent the values for these quantities when the

TABLE VII.

Length 35.5 *cm. Moment of Inertia* 3,611 *g. cm*².

March 24—III.			March 24—IV.			March 24—V.		
No.	Amp.	Period.	No.	Amp.	Period.	No.	Amp.	Period.
0	43.59	9.820	0	72.42	10.050	0	143.9	10.450
2	37.90	770	2	60.33	9.970	2	120.4	370
4	33.57	712	4	50.83	883	4	100.1	290
6	30.10	670	6	43.50	815	6	83.25	220
8	27.37	630	8	37.89	763	8	69.67	150
10	24.99	592	10	33.48	710	10	58.15	054
12	23.08	560	12	30.10	668	12	49.08	9.990
14	21.51	542	14	27.23	630	14	41.78	912
16	20.21	528	16	24.96	595	16	36.09	848
18	19.01	514	18	23.16	565	18	31.64	789
20	18.06	503	20	21.62	541	20	28.11	732
22	17.16	493	22	20.35	520	22	25.32	688
24	16.40	486	24	19.16	505	24	23.16	650
26	15.69	480	26	18.16	494	26	21.26	617
28	15.05	473	28	17.31	484	28	19.80	593
30	14.52	468	30	16.52	474	30	18.41	572
32	14.03	460	32	15.82	468	32	17.31	556
34	13.56	453	34	15.20	460	34	16.38	542
36	13.14	449	36	14.68	455	36	15.48	531
38	12.78	443	38	14.17	450	38	14.73	521
40	12.40	440	40	13.71	445	40	14.10	511
71	9.13	413	90	8.45	403	76	8.54	448
100	7.37	404	123	6.87	394	102	6.79	434
127	6.35	398	154	5.94	388	130	5.64	427

distortions following the large one of 320° from the center were respectively 21.8°, 36.2° and 72° from the center, or in our present nomenclature double amplitudes of 43.6°, 72.4° and 143.9° respectively. Curve (*d*) is decidedly below (*a*), while (*b*) and (*c*) are below (*d*). The curves (*b*) and (*c*) seem to fall almost exactly together as far as they cover common ground. It would seem from this fact that there is a certain limiting amplitude below which it takes the wire a longer time to recover. In order to make certain of this last point, further experiments will be necessary. The rather complicated behavior of the wire is then brought out by these experiments; for a given amplitude we find that the period depends upon whether the wire has been freshly annealed or not,

upon whether it has approached the amplitude from a larger one or from a smaller one, and finally upon how long the wire has rested since its last distortion. There seems good reason to believe that with a long rest the wire might in great part regain its original condition. During the present investigation, however, there has been no opportunity to substantiate this point. From the results

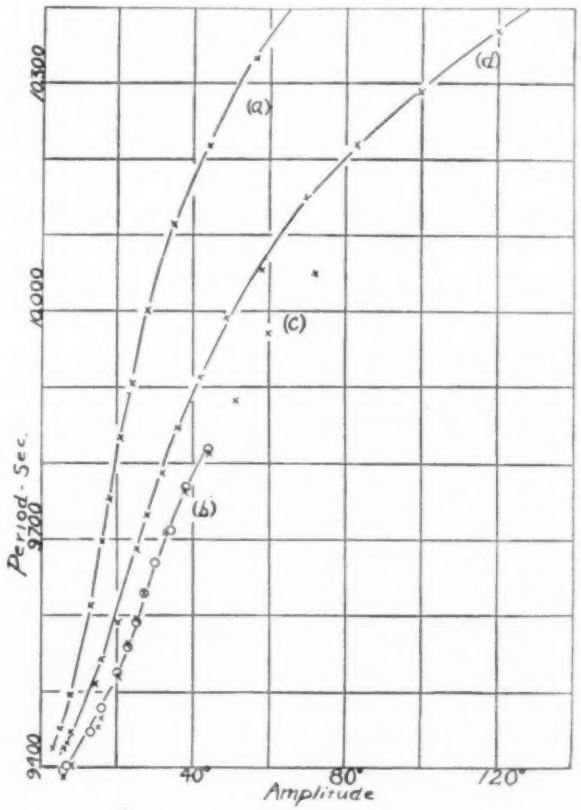


Fig. 6.

of the preceding observations, it is evident that experiments of other kinds upon this wire (for example the variation of the period with the moment of inertia of the suspended mass, the temperature coefficient, heat treatment, etc.) would be of little or no value unless a definite relation under varying conditions could be obtained between the period and the amplitude. It is true, that after anneal-

ing the wire with a current sufficient to bring it to a red heat a fairly definite relation between period and amplitude can with proper care be obtained. The annealing appears to destroy the previous history of the wire as far as elastic after effects are concerned. This method has been used in many of the experiments. However one must be extremely careful in the treatment of the wire after annealing it, as a single accidental vibration of even thirty or forty degrees is sufficient to change its condition most evidently.

3. *Attempts to Put the Wire in a Definite State.*—Since the method of annealing led to somewhat uncertain results, it seemed desirable to find another method of putting the wire into a definite state. To find the proper conditions, many experiments were attempted before what now seems to be the proper solution was found. Of these experiments only a few of the significant ones will be given.

In the first place an attempt was made to obtain the period at a given amplitude by keeping the pendulum vibrating at a fixed amplitude by means of the torsion head. It will be remembered that the wire dies down so rapidly that the period for a given amplitude can be obtained only by means of the tape and the chronograph, and even in this way only a single value is obtained, so quickly does the amplitude fall off. This ability to gain only a single value for the period might lead to the suspicion that the possible error in timing would vitiate any attempt at refined results. So the continued vibration at constant amplitude served two purposes: viz., to see if in timing by ordinary methods at constant amplitude there was any change in the period as time went on; and also to see if the periods obtained by finally letting the vibrations die down in the usual way (timing them with the chronograph and the tape) would join those obtained at constant amplitude without any break. The first point—the change in period resulting from continued vibration at constant amplitude—is brought out in Table VIII. In this table it appears from the experiment of November 2, that the period gradually increased from 5.875 sec. to 5.886 sec., while the amplitude was held within 2 or 3 degrees of 269 degrees, and it appears also, from the experiment of November 5, that the period increased from 5.900 sec. to 5.908 sec., while the amplitude remained at 299 degrees.

TABLE VIII.

Length 40.2 *cm.* *Moment of Inertia* 980 *g. cm².* *Amplitude* 269°.

Coincidences.	Interval 'sec.).	No. of Vibrations.	Period.
3h 20m 32s			
22 06	94	16	5.875
27 00	388	66	.879
28 34	482	82	.878
32 06	694	118	.881
35 50	918	156	.885
39 34	1142	194	.886
46 26	1554	264	.886
		Amplitude 299°.	
5h 3m 28s			
5 26	118	20	5.900
9 34	366	62	.903
11 44	496	84	.905
13 54	626	106	.906
18 26	898	152	.908
20 36	1028	174	.908
22 46	1158	196	.908

Further information on this point is shown in Table IX., based on a set of experiments taken in such close succession that the wire was kept in almost continuous vibration. To be exact, the wire was vibrated 23 minutes, rested 22 minutes, vibrated 28 minutes, rested 14 minutes, and finally vibrated 24 minutes. During the periods of rest the wire was not wholly quiet, for it was during these intervals that the stops on the torsion head were adjusted for the new amplitudes, and many trials were necessary before the desired amplitudes could be reached and maintained. So it can be stated correctly that the vibration continued practically two hours. This may seem a trivial point, but later experiments have shown its importance.

In this table are recorded data for experiments at three different amplitudes. During this group of experiments the temperature was constant within about 1° C.; it might be added here that the same care as to constancy of temperature was observed in each set of experiments. The three experiments in this group showed some interesting results. It will be noticed that for the amplitude of

TABLE IX.

Length 40.2 *cm.* *Moment of Inertia* 980 *g. cm*^{2}. *Amplitude* 825°.

Coincidences.			Interval (sec.).	No. of Vibrations.	Period.
10h	53m	56s			
	59	10	314	52	6.032
11	3	24	568	94	.048
	7	2	786	130	.055
	10	28	992	164	.059
	13	42	1,186	196	.063
				Amplitude 748°	
11h	38m	44s			
	41	34	170	28	6.071
	44	24	170	28	.071
	49	40	316	52	.077
	54	44	304	50	.080
	59	48	304	50	.080
12	4	40	292	48	.083
				Amplitude 579°	
12h	21m	6s			
	24	8	182	30	6.067
	27	22	194	32	.063
	33	14	352	58	.069
	33	16	182	30	.067
	39	6	170	28	.071
	41	56	170	28	.071
	44	58	182	30	.067

825 degrees the period increases from 6.032 sec. to 6.063 sec., that for the amplitude of 748 degrees the period increases from 6.071 sec. to 6.083 sec., and that for the amplitude of 579 degrees the period is practically constant and smaller than in the other two experiments. The fact that, in the third experiment the period is lower, is not unreasonable as all of the preceding experiments have indicated shorter periods at the smaller amplitudes; and though accompanying the fall in amplitude from 825° to 748° there is an actual rise in the period, still this rise could not well continue indefinitely. Ultimately at some amplitude the rise in period would cease, and the period would fall off. This rise in the period due to continued vibrations at a given amplitude, or even at a somewhat smaller amplitude, will be further discussed in a following section.

However the important point now is that the period seems to have reached, in this third experiment, practically a constant value for the given amplitude. There are, of course, variations due very probably to errors of observation, but admitting even the maximum variations in the periods, the percentage changes in the three cases are respectively, 0.52 per cent., 0.20 per cent. and 0.15 per cent. Obviously, the deduction is that a fair constancy of period for a given amplitude can be obtained only after the wire has been vibrated for some time.

The second purpose of the above experiment was, it may be remembered, to test whether or not the periods obtained when the torsion head was stopped and the wire allowed to die down in the usual way, follow without any break the periods obtained by coincidences. A comparison of Table VIII. and Table X. will make this point clear. In Table VIII. (lower half) are recorded the periods,

TABLE X.

Length 40.2 *cm.* *Moment of Inertia* 980 *g. cm².*

No.	Amp.	Period.	No.	Amp.	Period.	No.	Amp.	Period.
0	292	5.898	25	116	5.850	70	7	5.441
2	277	898	30	92	822	75	6	415
4	260	897	35	67	786	80	5	403
6	244	895	40	48	730	85	5	395
8	230	894	45	35	672	98	3.59	376
10	214	892	50	24	615	119	2.27	333
12	199	890	55	17	560	149	1.67	333
15	177	885	60	12	515	179	1.16	333
20	147	870	65	9	473			

obtained by coincidences, where the vibrations had been held at constant amplitude. The subsequent periods of this same torsion pendulum, as it died down naturally, are given in Table X. It is evident that these latter periods join the former periods without any serious break.

In most of the experiments performed, the amplitudes were not taken below one degree, and very commonly not below two degrees. This was usually because a small side swing had developed as a result of the disturbances incident on setting the pendulum into the

large vibrations. While these small side swings did not appreciably vitiate the results for amplitudes down to five or six degrees, they made it impossible to get accurate readings much below this point. Many of the curves for amplitude and period seemed to indicate that at low values for the amplitude there was a tendency towards constancy in period. This point was tested by several carefully performed experiments at small amplitudes. The damping was so small here that the periods could easily be obtained by the method of coincidences. The results are given in Table XI., and in Fig. 7.

TABLE XI.

Length 40.2 *cm. Moment of Inertia* 980 *g. cm*^{2}.

Amp	Period.	Amp.	Period.
4.1	5.333	.91	.292
2.96	.321	.75	.290
2.3	.313	.68	.290
1.8	.308	.58	.288
1.3	.288	.50	.287
1.19	.296	.41	.286
1.07	.295		

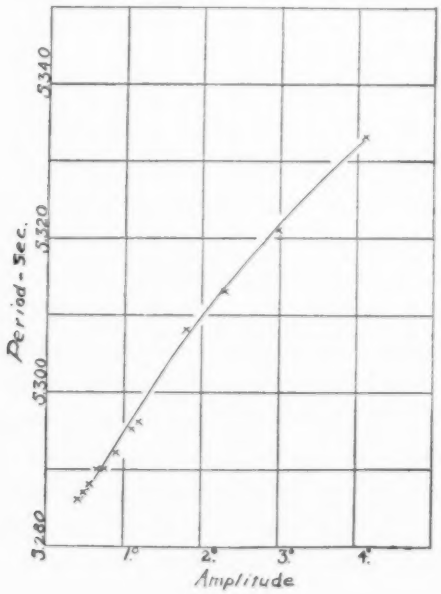


Fig. 7.

From these results it is evident that the relation between the period and the amplitude is, for these small values, a linear one, and that there is no evidence of constancy of period, at least not above 0.4 degree. Below this amplitude, it is very difficult to time with any accuracy.

4. *Effect of a Slow Torsion of the Wire through the Maximum Range of Amplitude.*—The next query that arose was whether the peculiar state of the wire caused by vibrating it through a large amplitude after annealing, was due merely to the amplitude of the torsional strain, or to some internal phenomena accompanying the actual vibration. This point was tested in the following simple experiment. The weight attached to the wire was firmly clamped. Then, after the wire had been annealed to red heat, the torsion head was slowly turned through 360 degrees. After being held in this position 30 seconds, it was twisted back to zero, and then on to the other side to the same amplitude. It was held there 30 seconds, and finally returned to the zero point. The weight was then carefully released, and the wire allowed to rest 24 hours, at the end of which time a regular experiment was made with an initial amplitude of 35 degrees. It was necessary to take this small amplitude, for otherwise the effect sought would have been lost in the complications that arise from the larger amplitudes. The results for period and amplitude are given in Fig. 8, curve (*c*), where for comparison two other curves covering about the same range of amplitudes are given; curve (*a*) illustrating an experiment where the wire had been freshly annealed, and curve (*b*) illustrating an experiment where the wire had been vibrated for some time at larger amplitudes. The results are very striking, and show clearly what effect the mere torsional strain has on the state of the wire. Here clearly this single twist does not cause as great an effect as do long continued vibrations, but still the single twist does cause a decided change. In the same figure (Fig. 8) are platted from the same experiments the variation of the logarithmic decrement with the amplitude, the curves corresponding to (*a*), (*b*) and (*c*) being marked (*a'*), (*b'*) and (*c'*). From these logarithmic decrements it is seen that the larger the frictional losses, the larger the variation in the period.

5. *Successive Observations without Preliminary Vibrations.*—It was

thought barely possible that, although the period for a given amplitude does depend upon the previous state of the wire, yet three observations taken in succession with no more vibration than necessary might yield results that would be essentially alike. While this solution of the problem would not be satisfactory, it still would serve to give useful comparative results on a short series of experiments. As might have been expected, perhaps, the desired constancy was not obtained: this will be evident from an inspection

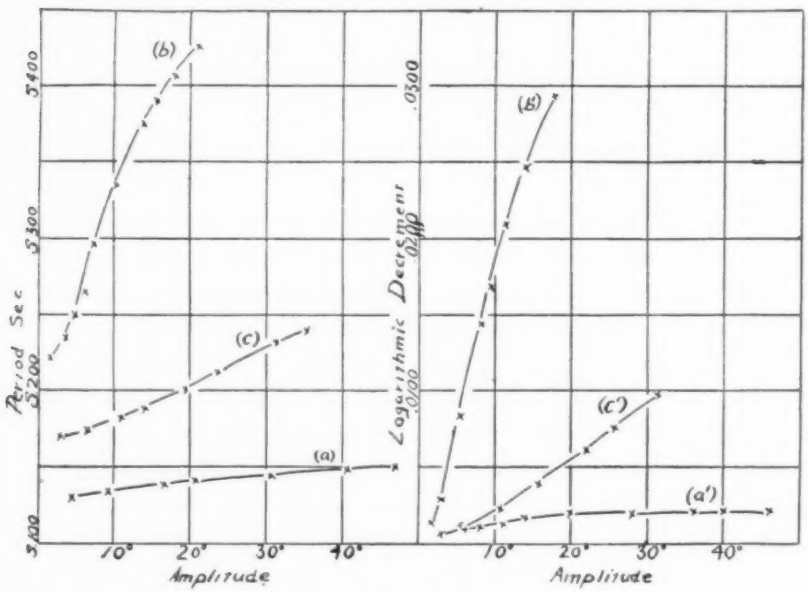


Fig. 8.

of Fig. 9 which represents the results of three successive experiments. The wire was annealed to red heat and set into vibration to its full amplitude by one single twist, then allowed to die down and timed. The results are given in curve (*a*). When this experiment had been completed, the wire was again set into vibration and timed. This was done a third time. These last two experiments are represented by the curves (*b*) and (*c*), respectively. The fact that the pendulum was put into vibration by means of one twist is mentioned because often before this it had been set into vibration by means of the

torsion head, by which the pendulum was twisted back and forth, "working it up" as it were.

This completed the first group of three experiments. As had been expected the results were unsatisfactory, yet it was thought best to repeat the three experiments varying, however, the first one. Even by this varied method, small chance seemed to remain of getting results of any value. The wire was annealed and then,

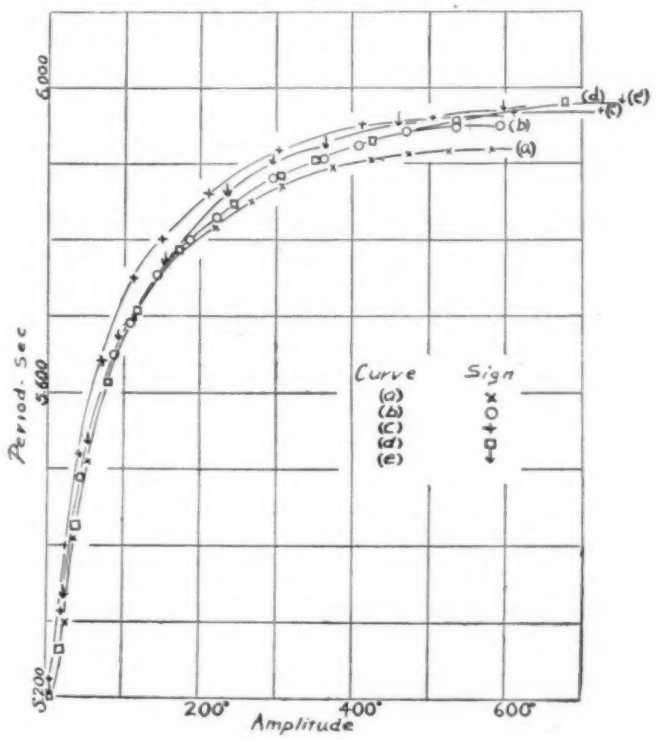


Fig. 9.

the weight being clamped, the torsion head was twisted as described above to the right 360 degrees, back to zero, then to the left, etc., and after that two observations were taken. It was thought that the variation in the period-amplitude curves as indicated in curves (*a*), (*b*) and (*c*), Fig. 9, was largely due to the first experiment, following the annealing. When the table of results (which for the sake of space is not given) was examined it was found that in the

two experiments the values of the periods for both the maximum and the minimum amplitudes were practically the same. In the first experiment (curve (*d*), Fig. 9) after the wire had been annealed and twisted, the range of periods was from 5.980 sec. to 5.200 sec., where the maximum amplitude was 677 degrees; in the second (curve (*e*), Fig. 9) the range in period was the same, while the maximum amplitude was 751 degrees. However when all the values were platted, the two curves were found to be decidedly different in form, as is evident from an inspection of curves (*d*) and (*e*). This general tendency of the curves to show, after repeated vibrations, a sharper curvature in the region where they bend over toward the amplitude axis, has been frequently observed.

6. *Effect of Long-continued Vibration on the Logarithmic Decrement-amplitude Curves.*—Along with this variation of the period-amplitude curves following continued vibrations, it is interesting to notice

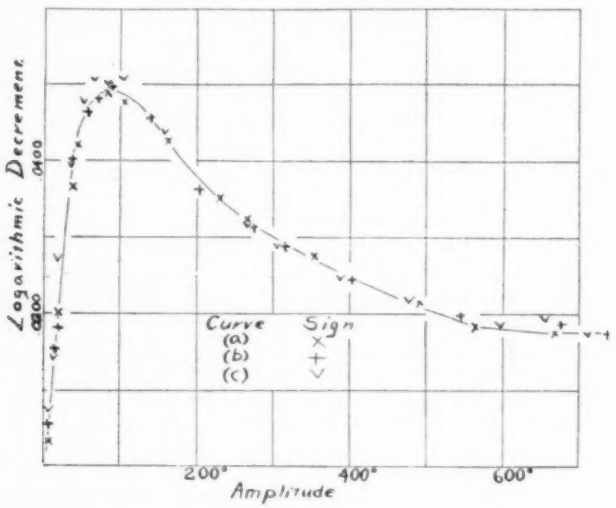


Fig. 10.

the corresponding variations of the logarithmic decrement-amplitude curves. To give but one illustration of this point, there are platted in Fig. 10, three curves, based upon three experiments performed on the same day, for the variation of the logarithmic decrement with the amplitude. The conditions governing these experiments

were as follows: The wire, being first annealed to red heat, was turned through 360° and timed. Curve (*a*) represents the variation of the logarithmic decrement. The wire was next vibrated by means of the torsion head through a total amplitude of 720° for 30 minutes and was then allowed to die down and was timed as usual. Curve (*b*) represents the variation of the logarithmic decrement. Lastly the wire was again vibrated as explained above, for 30 minutes. The values of the resulting decrement as the wire died down are given in curve (*c*). It is quite evident that the repeated vibrations had increased the internal friction of the wire, as the decrement, to a slight extent, progressively increased.[1] This increase of the decrement as well as of the period, following repeated vibrations, was first announced by Lord Kelvin[2] who experimented particularly with copper wires. J. O. Thompson[3] later showed that as long as the amplitude and temperature remain constant there is no change in the period or in the logarithmic decrement. Still later this same phenomenon was found by Bouasse[4] to hold for repeated vibrations on a hard drawn copper wire. He expressed the belief that this change did not come through a change in the elasticity, but through a change in the cohesion of the molecules of the wire.

7. *Long-continued Vibrations.*—The last step, and the one that seems to have given a solution of the problem of this paper, was to vibrate the wire for much longer periods than hitherto, before taking observations on the relation between period and amplitude. Had the information recorded in the earlier sections of this paper been previously known to the writer, this method of treatment would have been arrived at much sooner. The following figure (Fig. 11) represents the results of the variation of period and amplitude for ten experiments to be described, but to save confusion in the curves, with the exception of the results from two experiments, only the values of the periods for amplitudes above 300 degrees are given.

[1]H. G. Tammen [Carl Rep., 18, p. 350, 1882] found with copper wire an increase of the log. dec. for a given amplitude with the duration of the vibration. He found also a *decrease* in the log. dec. with increase in the amplitude.

[2]Kelvin, Math. and Phys. Papers, III., p. 26.

[3]J. O. Thompson, PHYS. REV., 8, p. 141, 1899.

[4]H. Bouasse, Ann. Chim. Phys. (8), 2, pp. 5–77, 1904.

In the same figure the values of the periods for the smaller amplitudes are given on a larger scale for some of the experiments, the primes of the same letters being used to indicate the large-scale curves. The wire was first annealed, and started to vibrate at an amplitude from the center of 360°, the results being given in (*a*). Then the wire was vibrated through a nearly constant amplitude of 720 degrees for 30 minutes, and the results of the subsequent

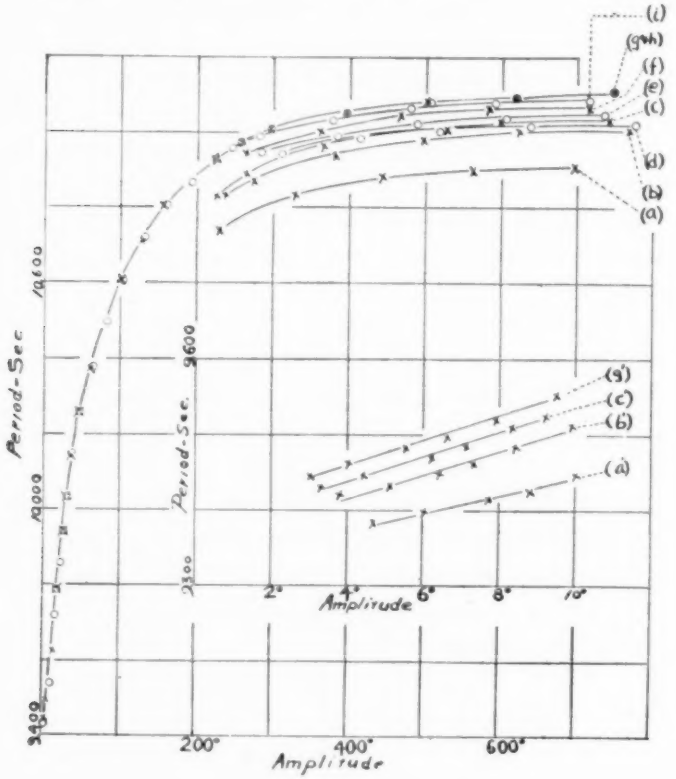


Fig. 11.

experiment as the wire died down are shown in (*b*), where a decided increase in the period is to be observed. Next the wire was vibrated for another 30 minutes. Curve (*c*), representing the results, shows a still higher period. The wire was now allowed to rest for one week, and without preliminary vibration, the usual experiment was tried. As was to be expected from previous results, the wire's

period had, due to the week's rest, fallen back slightly; the results are shown in (*d*). The pendulum was now vibrated an additional 30 minutes, and then was given a second vibration of 30 minutes. The results of these two vibrations are given in curves (*e*) and (*f*) respectively. It began to seem as though the pursuit of an upper limit for the period would be hopeless unless stronger measures were taken, so after a three days' rest the pendulum was kept in continuous vibration for two and one half hours.[1] The results of this experiment are given completely in (*g*). After this observation the wire was at once twisted to the maximum amplitude. The observation for the succeeding periods is recorded in curve (*h*), which agrees with (*g*) throughout the entire range. Curve (*i*), the record for an experiment performed two days later, shows the usual tendency of the period to fall off after an interval of rest. An objection to the above experiments is that following (*g*) the pendulum was not vibrated a longer time before (*h*) was taken, for it could be argued that there might still be a further rise in the period. The objection may be well founded; but what was obtained was really what was sought, viz., to get a period-amplitude curve that could be, within the limits of error in timing, exactly duplicated. The almost exact duplication of curve (*g*) by curve (*h*) seems then to show that the wire, at least for the time being, had reached a definite and final condition. Further experiments on this point are planned for the near future.

IV. Effect of Variation of Moment of Inertia on the Period-Amplitude Curves.

In the former paper,[2] it was found that the nature of the period-amplitude curves was not appreciably affected by a variation in the moment of inertia of the suspended weight. Since in the earlier investigation no especial precautions were taken to eliminate the past history of the wire, there was a possibility that the effect of variation of moment of inertia was so small that it might have been masked by the irregularities resulting from the past treatment

[1] H. Streintz (Carl Rep., 16, p. 476, 1880) found that a definite elastic condition for ordinary wires was not reached even after they had been vibrated for three and one-half months.

[2] Guthe and Sieg, *loc. cit.*

of the wire. This the present investigation attempts to guard against. In all the preceding experiments mentioned in this paper the moment of inertia of the suspended weight was always the same in any one set of observations, so that its effect was a constant one. In the present observations four different cylinders, agreeing in mass (mass = 229 gr.) within 0.5 gram were used. The values of their moments of inertia, including that of the central supporting rod and the double mirror, were respectively: *A*, 3,611 c.g.s.; *B*, 980 c.g.s.; *C*, 474 c.g.s.; and *D*, 367 c.g.s. In each case the wire was annealed to red heat with a current of 2.5 amperes, and no preliminary vibrations were taken. With proper care this method was found in any given case to give consistent results. The curves, in order to be compared, had to be platted on different scales, since of course the periods varied with the different cylinders used. What amounted to the same thing as changing the scales used was to make the four results agree at some one amplitude, and then to use the factor thus determined to multiply all the values of the period in any one set. Some care has to be used here in choosing the proper amplitude at which to make comparisons. At first it was attempted to make all the periods agree at an amplitude of five degrees, but this led to serious variations, and the explanation was quite natural. At an amplitude as small as five degrees, or even in that neighborhood, the variation of the period with the amplitude was extremely large, and a slight error in properly choosing the true period at this amplitude made a large error in the corrected periods, especially in the cases of the cylinders of smallest moment of inertia. On the other hand it was undesirable to match values of the period at the largest amplitudes, because in the method of timing used these values were least accurate. In short, the amplitude of 500 degrees was taken as the point of reference because this amplitude was in a part of the curve far enough from the beginning to warrant accurate results, and still in a part of the curve where the variation of period with amplitude was small. A period of ten seconds was taken in each case for this amplitude, and the factors properly chosen to make all four curves agree at this point. The results are given in Table XII., and are graphically shown in Fig. 12, where the curves corresponding to the different cylinders

TABLE XII.

Length 36.1 *cm. Moment of Inertia: A* 3,611, *B* 980, *C* 474 *and D* 367 *g. cm*^{2}.

Cylinder A.			Cylinder B.		
Amp.	Period.	Corrected Period.	Amp.	Period.	Corrected Period.
735	11.141	10.006	741	5.720	10.017
515	.132	.000	500	.710	.000
500	.126	.000	485	.709	9.999
341	.096	9.968	375	.694	.972
310	.084	.956	261	.653	.901
281	.070	.944	242	.644	.885
252	.051	.927	210	.620	.843
226	.030	.907	165	.580	.773
200	.002	.882	140	.547	.716
165	10.955	.832	129	.525	.676
154	.931	.819	98.3	.466	.573
131	.890	.782	75.4	.415	.484
111	.810	.710	53.2	.334	.342
83.4	.689	.602	35.6	.240	.214
76.	.638	.556	25.6	.170	.055
50.2	.487	.420	16.1	.082	8.900
41.	.391	.412	9.37	.028	.806
20.2	.114	.162	7.2	.012	.782
5.29	9.721	8.805	5.0	4.998	.754
2.44	.644	.735	3.71	.989	.738
Cylinder C.			Cylinder D.		
826	3.964	10.025	890	3.488	10.032
675	.961	.018	730	.484	.020
540	.958	.010	591	.480	.009
500	.954	.000	500	.477	.000
312	.926	9.929	356	.461	9.954
272	.913	.896	312	.451	.925
199	.888	.823	237	.429	.862
166	.862	.767	201	.411	.810
137	.837	.704	168	.398	.773
111	.809	.633	138	.375	.707
90.4	.773	.542	112	.350	.635
73.1	.733	.441	91	.322	.554
53.8	.685	.320	74	.291	.465
44.1	.650	.231	60.5	.260	.376
33.9	.603	.112	49.5	.233	.298
22.3	.529	8.925	37.6	.194	.186
8.2	.450	.725	17.1	.078	8.852
7.0	.438	.695	10.8	.042	.749
5.0	.430	.674	5.00	.013	.666
2.50	.415	.637	2.20	2.998	.623

are clearly indicated on the figure. It is evident that although the curves are in general much alike, there still is a change that progresses with the change in the moment of inertia of the vibrating system; the larger the moment of inertia, the more tendency for the curves to remain parallel to the amplitude axis and the more abrupt the final bend toward the period axis. The curves are so

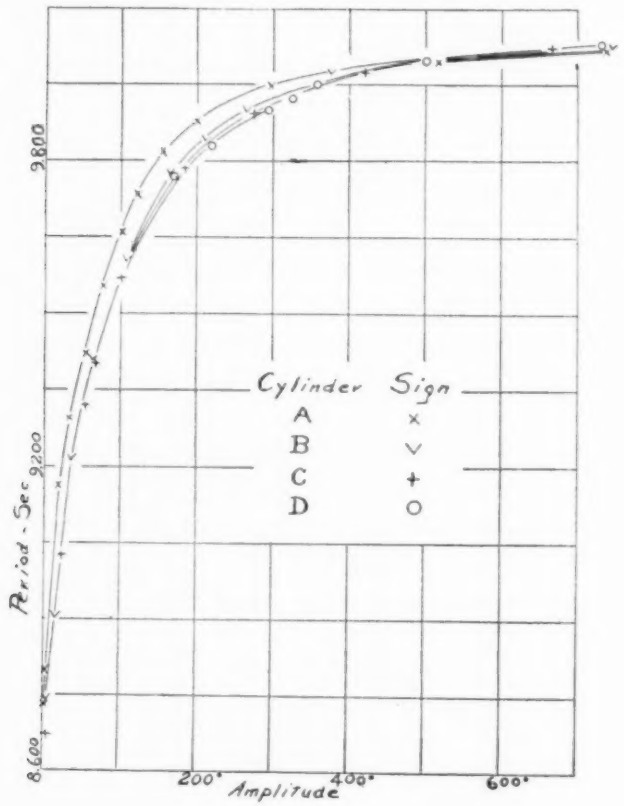


Fig. 12.

nearly alike that it is certain that this whole effect of variation of period with amplitude is largely a function of the amplitude only, but it is equally certain that the velocity of the vibration is a determining factor, even though a small one.

V. Determination of the Coefficient of Rigidity.

One obvious explanation of the remarkable variation in the the period-amplitude curves, would be to assume that with increased amplitude Hooke's law falls off as the period increases. This point was tested in the experiments recorded in the former paper,[1] by balancing different torques of the platinum-iridium wire against the torques of a steel wire. Assuming that the steel wire followed Hooke's law perfectly, then the wire in the above-mentioned investigation likewise followed the law up to the widest range of amplitudes used. To verify the above point, and to obtain a value for the coefficient of rigidity, measured statically, it was thought well to repeat this experiment by a more absolute method and one independent of any other wire. The method was to balance the torque of the wire by the couple caused by the bending of two delicate glass fibers. The fibers were drawn, and the end of each bent into a sharp hook. Then the two fibers were supported exactly as they were to be used in the experiment, calibrated by suspending small milligram weights from the hooks at the ends, and the resulting deflections read with a traveling microscope. In the final experiments on the wire, a microscope was used for each fiber. In calibrating the fibers and in the actual experiments with the wire, the deflections of the fibers were always small enough to follow Hooke's law almost perfectly. It was impossible to draw two fibers of exactly the same rigidity, but in all cases the two torques constituting the moment were made so nearly alike that the wire was undeviated from the cross wire of a reading telescope. Table XIII gives a résumé of the trials made. In the first column, under the heading $\theta°$, is the torsional strain in degrees from the position of rest. In the second and third columns, under f_1 and f_2 respectively, are the forces exerted on the two fibers, expressed in milligram weights. In the fourth column, under the head of torque (c.g.s.), is the torque in dyne-cms. obtained by multiplying the sum of f_1 and f_2 by 980 and by the radius of the cylinder to which the glass fibers were attached by silk threads. In the last column under the heading torque/$\theta°$ is the torque per degree of torsional

[1]Guthe and Sieg, *loc. cit.*

TABLE XIII.

$\theta°$	f_1 (mg. wt.)	f_2 (mg. wt.)	Torque (c.g.s.)	Torque/$\theta°$.
36.90	41.19	70.64	192.7	5.568
37.24	49.97	70.36	207.4	.582
38.17	43.60	80.00	213.1	.239
40.18	42.56	79.55	210.5	.223
143.6	290.7	159.5	776.1	.404
233.4	240.5	448.9	1,188.	.092
308.6	477.6	469.8	1,633.	.292
313.0	390.8	591.2	1,693.	.408
349.8	701.8	428.4	1,948.	.570
372.8	629.2	497.1	1,941.	.207
380.6	540.3	577.8	1,927.	.064
382.0	630.5	553.9	2,042.	.345
384.5	659.7	529.1	2,049.	.330
463.1	737.1	733.5	2,535.	.474
525.4	870.5	698.6	2,705.	.148
530.7	727.4	861.8	2,740.	.162
710.0	994.9	1,224.0	3,825.	.388
				Mean 5.323

$$\frac{\text{mean torque}}{\text{radian}} = 305 \text{ c.g.s.}$$

strain. From these data it is evident that this method is not productive of as accurate results as the method involving the use of the iron wire, and in itself this method would not establish the truth of Hooke's law. However among the values for the torque per unit angle there seems to be no tendency either to increase or to decrease at the larger values of the amplitudes. Using the mean value for the torque per radian as 305 c.g.s., and substituting in the formula $n = 2LT/\pi r^4$, the value $7.63 \cdot 10^{11}$ dynes/cm^2. is obtained for n, the coefficient of simple rigidity. This is about equal to the value of n for wrought iron. Even granting an error as large as 5 per cent. the value thus obtained for n is decidedly different from any value obtained for a small amplitude by the method of torsional vibrations. The results in Table XIV. giving the values of n for the four different moments of inertia used, illustrate this wide variation. In each case two values are given, one (n_1) for an amplitude of 500 degrees and one (n_2) for an amplitude of 5 degrees. Two interesting facts are to be noticed: first, the coeffi-

TABLE XIV.

Radius of wire .00975 cm.

Cylinder.	Moment of Inertia.	Length.	T_1 (mean solar) for Amp. 500°.	T_2 (mean solar) for Amp. 5°.	n_1	n_2
A	3611 g.cm².	35.5 cm.	22.020	19.380	7.35×10^{11}	9.50×10^{11}
B	980	36.1	11.390	9.969	7.58	9.90
C	474	36.1	7.887	6.842	7.65	10.17
D	367	36.1	6.935	6.010	7.66	10.20

cient of rigidity thus determined increases as the moment of inertia decreases; and second, the value of n for 500 degrees is smaller than the value obtained for smaller amplitudes and is much more nearly the value obtained statically, than is the value obtained at the smaller amplitudes. This is turning the usual order of things topsy turvy. But it is only at large amplitudes that the wire approaches anything like a constant period, and with a constant period the wire tends to act more like an ordinary wire. It is well known that even for ordinary wires the value of n obtained in these two different ways is different,[1] and it would be interesting to see if these two values would more nearly agree at the larger amplitudes.

As has been stated in the paragraph above, from Table XIV. it appears that there are apparently two different tendencies toward increase in the value of n. The first tendency toward increase, following a higher velocity of vibration due to the use of smaller moments of inertia, seems to indicate that possibly there is in every case a dragging of the instantaneous center toward the direction of vibration, but that the closeness with which this center follows the displacement is less in the case of the rapidly moving cylinders than in the case of the slowly moving ones. If we postulate that the torsional restoring couple on the wire is proportional to the angular distance of the wire from this instantaneous center and not from the original zero, then in the rapidly moving cylinders this center is at any time during the outward motion, farther away from the angular displacement than it is in the case of the slowly moving

[1]H. Tomlinson (Proc. Roy. Soc. Lond., 43, pp. 88–108, 1887) found that for iron wire the kinetic determination of n was larger than the static by 2 per cent. A like but smaller change was found to hold for Pt., Ag. and Al.

cylinders. So the restoring couple would be greater and the apparent elasticity of the wire greater. If, on the other hand, the observations be confined to any one cylinder, it is to be noted (Table XIV.) that the value of n increases with the smaller amplitudes. This exemplifies the second tendency mentioned above, and would seem to indicate that for the smaller amplitudes there is little or no yielding of the instantaneous rest point from the average rest point, and that therefore the restoring couple is correspondingly larger. This observation should be repeated with more widely varying moments of inertia.

VI. HEAT TREATMENT.

The following experiments are to be regarded merely as preliminary observations to indicate problems for future work on wires of this type. In the first place the question arose as to the effect of the annealing current, and as to what current, and hence what temperature, was necessary to restore the wire to the perfectly annealed condition. The first part of this present paper indicated that when the wire had been annealed, then vibrated through the usual amplitude of 360 degrees from the center, and then finally vibrated through a smaller angle, the change in period with amplitude was much larger for this small amplitude than it would have been if the preliminary large vibration had not occurred. The procedure in this present set of experiments was the following: (1) The wire was annealed to a bright red heat; (2) with a single twist, the suspended weight was turned through a displacement of 360 degrees from the center, and allowed to die down without timing; (3) a certain measured current was sent through the wire, care being taken not to allow any vibration during this process; (4) the pendulum was set into vibration through an amplitude of about 50 degrees, and timed in the usual way as the vibrations died down. No larger vibration than 50° was used, because a much larger value would annul the restoring effect of the current. This procedure constituted one experiment. In the next experiment, the first two steps were the same as those given above; the third step was the heating of the wire by a slightly larger current; the fourth step was the same as above. This was repeated with currents in

the third step ranging in value from zero to an intensity sufficient to raise the wire to red heat. In Fig. 13, in curves (*a*) to (*j*) inclusive, are given the results of this set of experiments, while in Table XV. are given for the corresponding curves the currents sent through the wire, and the resulting temperatures.

TABLE XV.

No.	Curve.	Current (Amperes).	Temperature (deg. Cent.).
1	*a*	0.00	22
2	*b*	0.50	72
3	*c*	1.02	205
4	*d*	1.21	262
5	*e*	1.29	290
6	*f*	1.38	318
7	*g*	1.47	406
8	*h*	2.03	648
9	*i*	2.50	851
10	*j*	2.70	930

In Fig. 14 are given the values of the logarithmic decrement for the preceding set of observations. It will be noticed in both figures that between curves (*d*) and (*e*), there has been a rapid change in both decrement and period accompanying a small increase in the temperature of the wire. Reference to Table XV. will show that the temperature corresponding to curve (*d*) was about 262 degrees, and that the change in temperature between that curve and (*e*) was only 28 degrees. It seems that a certain critical point had been reached in the neighborhood of these values. This is a fact that will receive further consideration. The temperatures were determined by an indirect method, but still by a method sufficiently accurate for preliminary experiments. The method used will be merely outlined. To equalize the effects of radiation, the room was kept at the same temperature that existed during the foregoing experiments. Various currents, covering more than the range used in the preceding experiments, were sent through the wire, and the fall of potential over the wire was measured by a potentiometer method in which the accuracy of the readings depended ultimately upon resistance readings. The current and the fall of potential

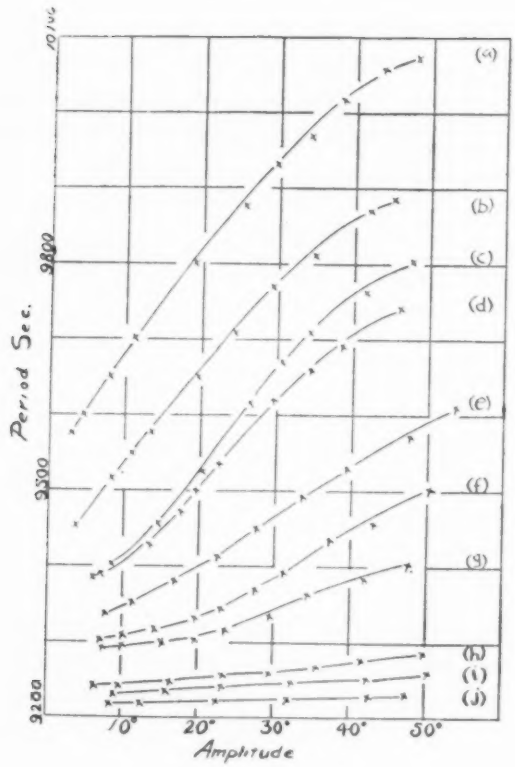

Period Sec.
.9400
.9300
.9200
10°
20°
30°
40°
50°
Amplitude
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)

Fig. 13.

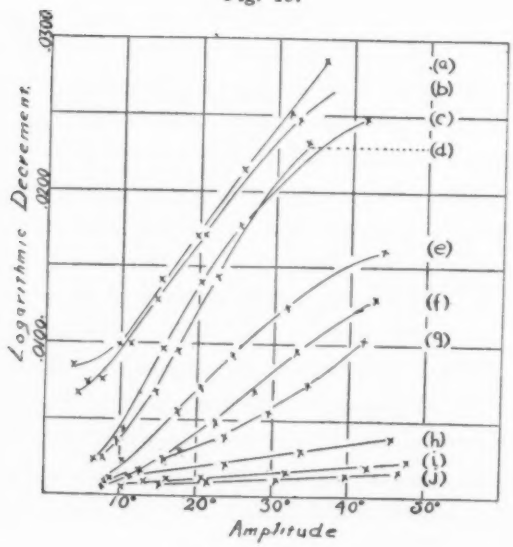

Logarithmic Decrement.
.0300
.0200
.0100
10°
20°
30°
40°
50°
Amplitude
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)

Fig. 14.

being known, the resistance could easily be calculated. This gave a graph of current and resistance. Then the wire was immersed in a bath of paraffin and the resistance for temperatures up to 280° C. determined. For values of the temperature above this point, the wire was removed from the paraffin, and calibrated by noting the melting points of crystals, observed under the microscope. The most satisfactory crystals used were sodium sulphate and potassium sulphate. The melting point of the former was taken at 880° C., and of the latter at 1066° C. In this way a graph for temperature and resistance was obtained which, within the limits of error, was a straight line. With these two curves, one for resistance and current, and the other for resistance and temperature, it was of course simple to construct a graph of temperature and current.

It was thought desirable to determine the variations in the period-amplitude curves which the wire showed at different temperatures, and for this purpose an electric furnace was constructed. It was realized that to get any accurate results the entire vibrating system should be enclosed in the furnace, with a window provided for reading the periods and the amplitudes. However as time was lacking, as only preliminary results were aimed at, and as such a furnace as that described above was difficult to construct on short notice, a temporary heater was used which enclosed only the wire. This unfortunately proved quite inadequate, for on account of the necessary clearance at the top and the bottom, unavoidable convection currents were set up. While the results were probably not far in error at the lower temperatures, at the higher ranges there was such a wide variation in the temperatures at the different parts of the furnace that the results obtained were worthless. There was another source of error in these experiments, which was not realized at the time they were performed, and that was in connection with point mentioned in the earlier part of the paper. During the set of experiments with the furnace, the wire was not annealed after being set in position in the heater, and as such a procedure would lead to a gradually increased period, and as an increase in temperature would lead undoubtedly to the same general change in the period, the results obtained, even with a perfect furnace would be of no particular value. The proper procedure, granting a satisfac-

tory furnace, would be to anneal the wire to exactly the same temperature before each experiment, and then after the desired temperature had been reached to set the wire in vibration, always in exactly the same way. This method ought not only to give the temperature coefficient of the period at different amplitudes, but also ought to indicate whether or not there is any change with the temperature in the shape of the principal curves discussed in this paper. It is hoped that such an experiment can be tried in the near future.

VII. SUMMARY.

1. In a 40 per cent. platinum-iridium wire, the torsional period as a function of the amplitude depends to a marked degree upon the previous treatment of the wire. Various preliminary treatments and their effects are summarized below.

(*a*) If after annealing the wire at red heat observations for the relation of period to amplitude are taken, it is found, where the initial amplitudes in the several experiments are gradually increased, that there is an increasing range in the variation of the period, and that for any given amplitude there is an increase in the successive values for the periods. In this same set of observations, it was found that up to a certain amplitude the number of vibrations occurring while the pendulum dies down to an amplitude of 5 degrees steadily diminishes, notwithstanding the fact that the amplitudes continually increase. The values of the logarithmic decrements as functions of the amplitudes, increase with the increasing amplitudes, and at a certain amplitude for a given experiment this function reaches a maximum.

(*b*) If the order of the above experiments is reversed, *i. e.*, if the original amplitude is gradually diminished, the curves for period and amplitude as long as they pass over common ground are much more nearly alike than they were in (*a*) above. There is also in this set (*b*) a marked agreement among the logarithmic decrement curves. Finally, the number of vibrations occurring while the pendulum dies down to 5 degrees, is less the smaller the initial amplitude.

(*c*) If the general method outlined above is varied by following the large initial amplitude immediately with a very small amplitude,

a noticeable difference in the results is obtained. In this last experiment with the small amplitude, the period-amplitude curve is decidedly below the curve obtained in the experiment with the large amplitude, and further, the curves obtained by this gradual increase of the smaller amplitude tend to assume forms intermediate between those described in sections (*a*) and (*b*) above. This indicates a tendency for the wire to restore itself to the annealed condition after a short period of rest. This tendency was, to a certain extent, masked in the observations recorded under section (*b*).

2. A method of preliminary treatment of the wire was sought, which would put the wire invariably into such a state that similar successive experiments would each time give the same relation between period and amplitude. The facts observed as results of these attempts are summarized as follows:

(*a*) By keeping the wire in continuous vibration at nearly constant amplitude with the aid of the torsion, head it was found that the periods increased at first, but that after sufficient vibration they approached constant values.

(*b*) In observations of the period, when the wire was allowed to die down naturally it was found that by preceding any observation for a given amplitude by a long continued vibration of the wire at that amplitude, the period was increased. Likewise, as a result of these preliminary vibrations, the form of the period-amplitude curve was changed, the period maintaining high values to lower amplitudes, and then more rapidly falling off with the further decrease in the amplitude. The increase in the period for a given amplitude, and the change in the form of the period-amplitude curves following the preliminary vibrations did not go on indefinitely, but in the case observed, reached after a vibration of two and one-half hours, practically constant values.

3. With constant load, the variation of the moment of inertia had a small but noticeable effect on the form of the period-amplitude curves; the larger the moment of inertia, the stronger was the tendency for the period to keep at high values while the amplitudes were decreasing, and then to fall off very rapidly as the amplitudes reached the lowest values.

4. The coefficient of rigidity of the wire was determined by a

static method, and when compared to the values determined by the kinetic method was found to agree with the latter more nearly when the values determined kinetically were for larger amplitudes. For the small amplitudes the values determined by the kinetic method were larger than those determined by the static method. These observations are not in agreement with the results obtained by Guthe and Sieg, who employed another method, and the point should be investigated further. For the coefficient of rigidity for a given amplitude, the values obtained by the kinetic method were found to increase with decrease in the moment of inertia.

5. Some preliminary experiments were tried in which different currents were passed through the wire, after the wire had been annealed to red heat and vibrated through a large amplitude. It was found that the greater this current through the wire, the greater was the restoring action of the resulting increase in temperature. When the temperature of the wire was raised by this current to about 275° C., there seemed to have been a marked acceleration of this restoring power.

In conclusion, the writer wishes to express his appreciation of the help and suggestions received from Professor K. E. Guthe, who suggested the problem, and from Professor G. W. Stewart, both of whom throughout the work have shown a most helpful interest.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA,
April 18, 1910.

THE EFFECT OF TEMPERATURE ON FLUORESCENCE AND ABSORPTION.

By R. C. Gibbs.

III. Absorption of Various Specimens at High Temperature.

THE effect of high temperature on the absorption of the specimens described in this paper is a continuation of the work done on uranium glass at high temperatures[1] and at low temperatures.[2] The substances investigated consisted of various colored glasses of unknown composition, a few cubes, the composition of which was partially known, and a cube of fluorite. Only a few of these specimens showed any fluorescence.

Apparatus.

The specimen G was placed inside a hollow iron cylinder, as indicated in Fig. 16. On the outside of the cylinder was wound a few layers of iron wire and heating was secured by sending an electric current through this wire. The temperature of the specimen was measured by an iron constantan thermo-junction J. For convenience in inserting the specimen into the furnace, it was first placed inside of a cylindrical iron case C. This case fitted rather closely into the opening in the iron cylinder and was pushed into place by another hollow iron tube T, the inner cross section of which was slightly smaller than that of the case. In order to prevent internal reflection as much as possible, iron washers W_1 and W_2 were placed at each end of the iron case. To prevent air currents and therefore unequal heating, two mica windows were placed in positions indicated by M_1 and M_2. A hole was drilled in the side of the furnace for the purpose of observing the effect of high temperature on the fluorescence of the specimens studied and was filled with a plug P when the intensity of transmitted light was

[1] Gibbs, R. C., Phys. Rev., Vol. XXVIII., No. 5, p. 361.
[2] Gibbs, R. C., Phys. Rev., Vol. XXX., No. 3, p. 377.

being measured. Some of the specimens were thin pieces of glass and in order to hold them in position, they were ground to very nearly the same diameter as that of the iron case and inserted be-

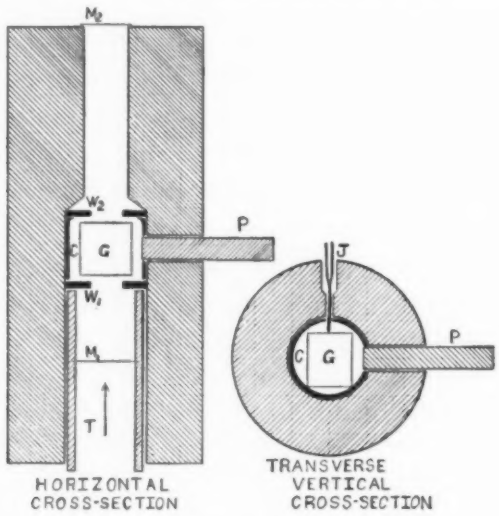


Fig. 16.

tween it and the washer W_1. The intensity of transmitted light was measured by means of the Lummer-Brodhun spectrophotometer. The arrangement of the apparatus is shown in Fig. 17.

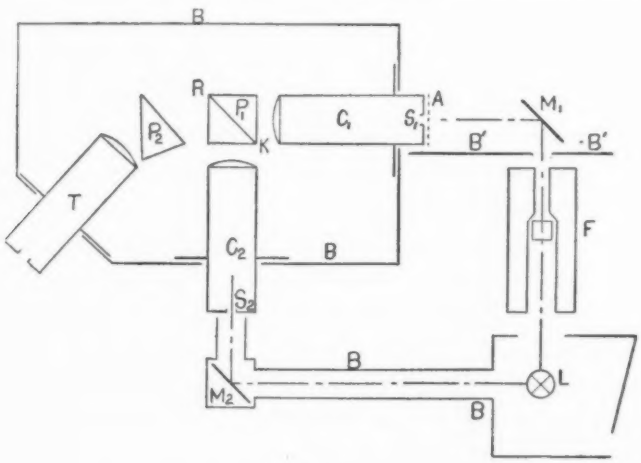


Fig. 17.

F represents the furnace, L the acetylene flame, M_1 a glass mirror and M_2 a block of magnesium carbonate, B screens covered with black paper, B' several layers of asbestos, covered with black paper on the side of the mirror, to prevent undue heating of the mirror, and A a ground glass screen to secure uniform intensity of field. Slit S_1 was set to a constant width in most of the observations and the intensity measured by varying the width of slit S_2. A set of observations throughout the spectrum was made with the glass removed from the furnace, and the intensity of the light thus measured was regarded as that of the incident light subject to corrections for reflection which will be mentioned later. The specimen was then inserted into the furnace and a set of observations made throughout that part of the spectrum where sufficient light was transmitted to be measurable. The temperature was then raised and a set of similar observations made at 100°, 200°, 300°, and 400° C., at which temperatures sufficient time was given to let the temperature inside of the furnace become uniform. After the measurements had been made at the highest temperature, the furnace was allowed to cool off and observations were made again at room temperature on the following day. This procedure seemed justifiable because the same acetylene flame served both for the source of incident light and that of the comparison light.

Correction for Reflection.

The ratio of the intensity of the transmitted light to that of the incident light measured, as mentioned above, would be the percentage transmission if it were not for the reflection at both surfaces of the specimen. In the case of normal incidence, about four per cent. of the light falling upon the glass surfaces is reflected. This is computed on the assumption that in the Fresnel formula $[(n-1) \div (n+1)]^2$, we use 3/2 for the index of refraction. This same percentage will be reflected at the second surface, so that if we regard I as the intensity of the light striking the first surface $.96I$ will actually get into the specimen. If we designate the observed transmitted light by T, the amount of light which reached the second surface of the specimen would be $T/.96$ and we should then have $T/I(.96)^2$ as the ratio of the intensity of the light reaching the

second surface to that of the light which entered the specimen, or in other words $T/I(.96)^2$ is the percentage transmission. Attention is here called to the fact that Kayser, in his Handbuch der Spectroscopie, Vol. III., p. 12, has failed to take account of the reflection at the second surface in the case of normal incidence. In the following results, the percentage transmission was computed

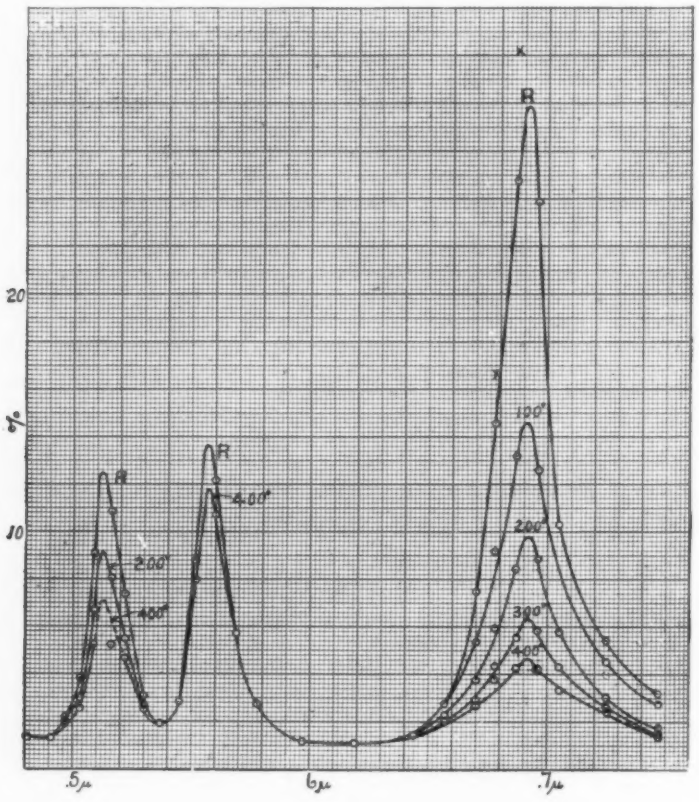


Fig. 18.

Showing the percentage transmission of erbium glass at various temperatures. Thickness = 1.451 cm.

according to the above formula with the full realization that the light did not strike all parts of the surface at normal incidence, and that the index of refraction is not 3/2 for all wave-lengths, but the error thus introduced is probably negligible.

Coefficient of Absorption.

The coefficient of absorption β, shown in the following curves, was computed from the formula

$$\beta = \frac{\log_e 1/D}{x},$$

where D represents $T/I(.96)^2$ and x the thickness of the specimen. The computations for the numerator of this formula were made graphically by referring to a curve which was secured by plotting between percentage transmission and the $\log_e 1/D$, the curve extending from small percentages up to 100.

Erbium Glass.

A specimen of glass found in the laboratory, which showed when viewed through a pocket spectroscope practically a line transmission spectra, was for various reasons thought to contain erbium, and its percentage transmission for various temperatures, is shown in Fig. 18. Inasmuch as the transmission bands are very narrow and the absorption bands so great, it was necessary to use a variable slit width and below is a table of the slit width in millimeters for the various wave-lengths.

Table IV.

λ	Slit Width.	λ	Slit Width.
.481μ	1.0	.578μ	.6
.491	1.0	.597	1.0
.497	.6	.691	1.0
.503	.6	.644	1.0
.509	.3	.657	1.0
.516	.3	.670	1.0
.522	.3	.678	.5
.530	.6	.687	.5
.537	.6	.696	.5
.545	.6	.705	.5
.552	.3	.725	1.0
.560	.3	.747	1.0
.569	.6		

Below is a table showing width of slit in terms of wave-lengths at various parts of the spectrum for a slit width of .7 mm.:

.450μ	7+$\mu\mu$	.600μ	21+$\mu\mu$
.500	11+	.650	27−
.550	16−	.700	35

The above slit widths were used for high temperatures except that for 300° and 400° the slit width was kept at 1 mm. throughout the red band. In computing the percentage transmission,

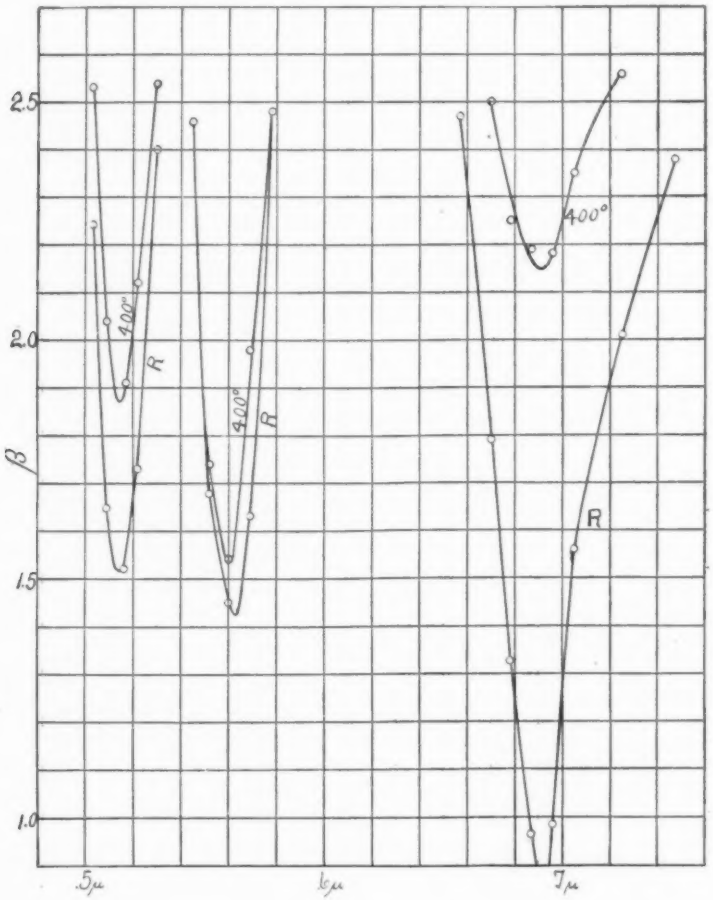


Fig. 19.

Showing coefficient of absorption of erbium glass.

the observed intensities of transmission were reduced to a standard slit width by assuming a strict proportionality between intensity

and slit widths which in several cases is probably far from true. It is however to be noticed that exceptionally smooth curves were obtained as the result of such procedure. Of course the small percentage transmission between the bright bands has no very great significance, as considerable of the light there measured might have been due to stray light, and in plotting the coefficient of absorption for this specimen, as shown in Fig. 19, only those bands which lie near the brighter regions of the spectrum have been indicated. With narrow bands of this sort considerable error is made, due to the width of the slit and two points are shown in Fig. 18 by crosses which indicate the nature and magnitude of the correction to be made, because of this error. The location of these points was determined by reference to the formula derived by Nichols and Merritt.[1] The luminescence curve of the comparison source necessary for computing this correction was obtained from data given by Abney and Festing.[2] In deriving the general formula for slit correction, a small mistake was made in the computation, and the authors have asked the writer to call attention to the error. On page 342 of this article, the coefficients of f and f'' were added and one of the coefficients $(c-a)^3/3$ was omitted. When this is introduced the value of k_1 becomes $c(a^2+c^2)/3$ when $a<c$, the same value as when $a>c$.

The intensity of the transmitted light decreases considerably in both the red and green bands, but shows a very slight decrease in the yellow band. On cooling back to room temperature, the intensity of transmitted light was the same as before heating. There seems to be no shift of the bands on heating and the coefficient of absorption curves serve to emphasize the narrowness of these transmission bands.

Sapphirin Glass.

In Fig. 20 is shown the percentage transmission for various temperatures on first heating this specimen. Up to 300° there is a slight increase in transmission in the neighborhood of the absorption band, especially on the side of the shorter wave-lengths, and a slight decrease in the transmission in the blue end of the spectrum. At

[1] Nichols and Merritt, Phys. Rev., Vol. XXX., No. 3, p. 343.

[2] Abney and Festing, Phil. Trans., 1886, II., p. 542.

400° the transmitted light had increased considerably at the red end of the spectrum, but decreased considerably in the region from the crest of the absorption band to the shortest wave-length measured. On cooling back to room temperature, the broken line in

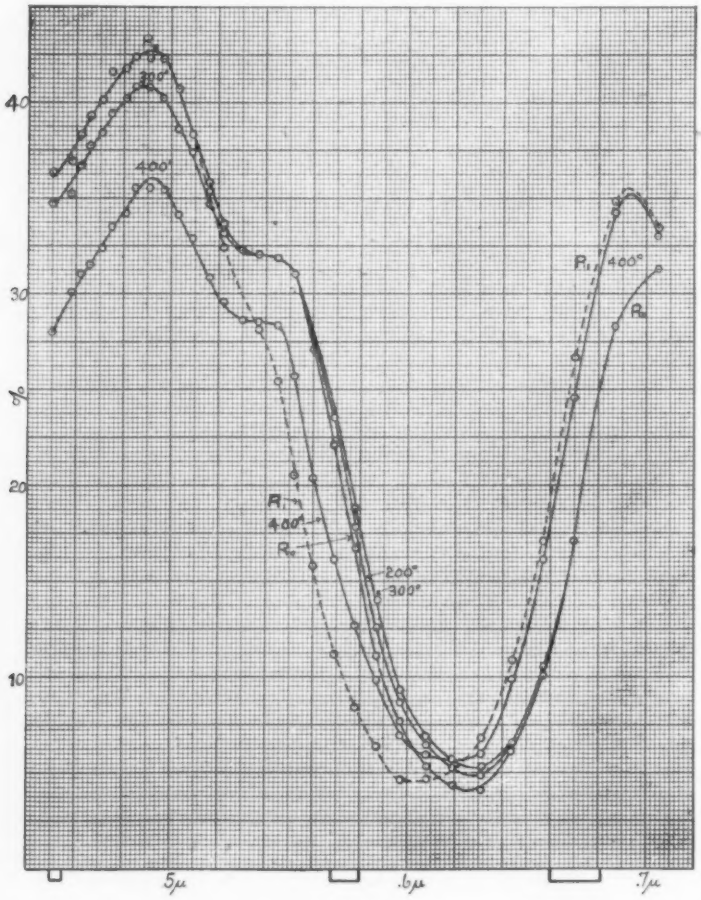


Fig. 20.

Showing the percentage transmission at various temperatures of sapphirin glass on first heating. R_0 = room temperature before heating. R_1 = room temperature after heating. Thickness = 1.344 cm.

Fig. 20 indicates the percentage transmission showing a considerable shift of the absorption band toward the shorter wave-lengths, a slight decrease in the maximum of the absorption and an almost

complete disappearance of the irregularity in the neighborhood of .54μ. The intensity was measured at room temperature on three successive days and it was found that the change above noted was a permanent one, at least for that length of time. The specimen was

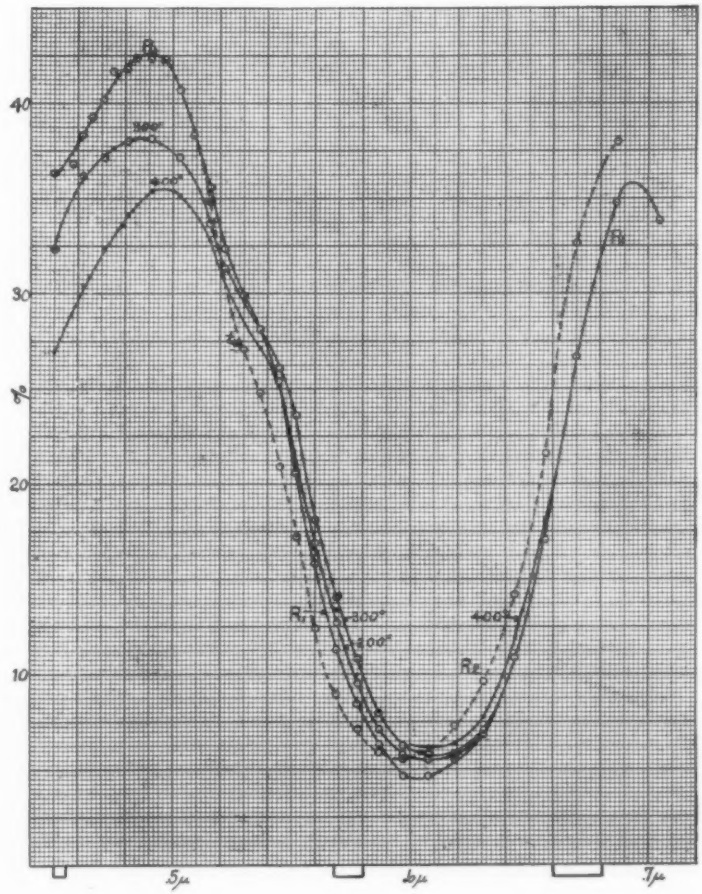


Fig. 21.

Showing percentage transmission of sapphirin glass at various temperatures on second heating. R_1 = room temperature before second heating. R_2 = room temperature after second heating.

again heated and in Fig. 21 are shown the corresponding changes which were very similar in nature to those on the first heating, but somewhat smaller in magnitude. The permanent shift was again

observed after cooling back to room temperature, although it was not so much as in the first case. The three room temperature curves are shown in Fig 22 and they seem to indicate that the glass on heating was undergoing some change analogous to annealing and would

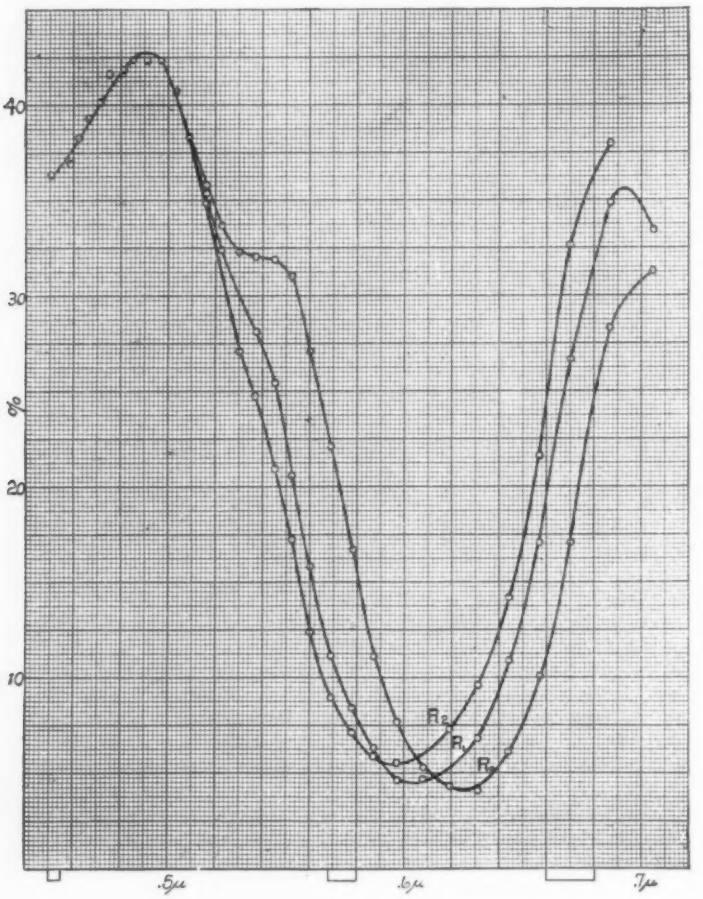


Fig. 22.

Showing percentage transmission of sapphirin glass at room temperature at three different times. R_0 = room temperature before heating. R_2 = room temperature after first heating. R_2 = room temperature after second heating.

probably reach a steady state after several heatings. Looking at the specimen directly with the eye, small colored streaks could be seen in the glass due to irregularities, and these show quite a dif-

ferent color after heating. This specimen shows a brick red fluorescence particularly when excited by daylight, but a very small amount of fluorescence, if any, when excited by the light of the mercury arc. The effect of heating on the fluorescence seemed to

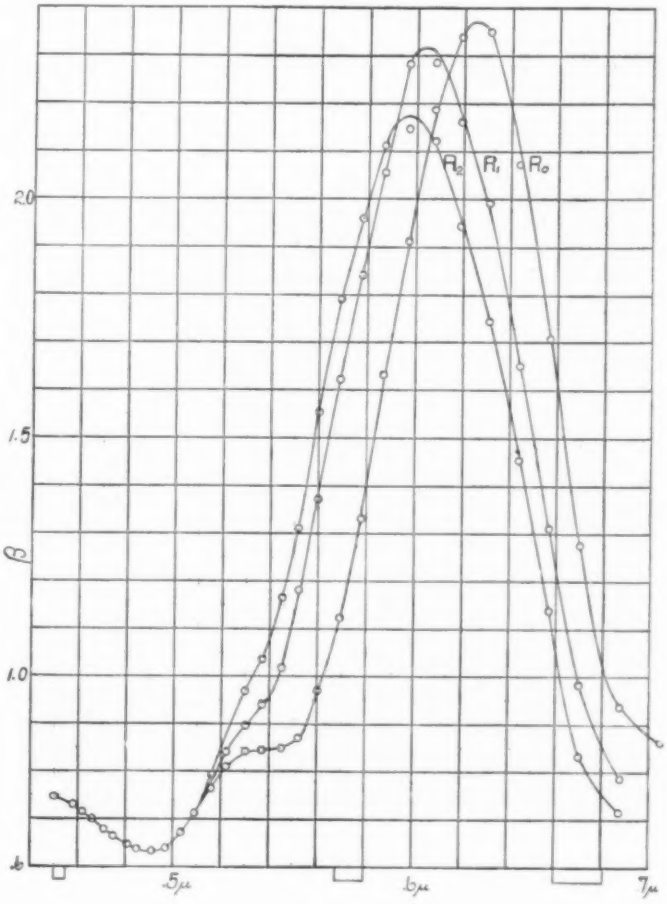


Fig. 23.

Showing coefficient of absorption of sapphirin glass at room temperature. R_0 = room temperature before heating. R_1 = room temperature after first heating. R_2 = room temperature after second heating.

increase its intensity. This was, however, determined by looking at this specimen directly with the eye through the hole made in the side of the furnace, and is not to be regarded as very accurate.

In Fig. 23 is shown the coefficient of absorption for the three room temperature measurements. In the last four figures, as well as in the figures that follow, the little rectangles at the bottom indicate the width of slit in wave-lengths.

COBALT GLASS NO. 1.

In the curves in Fig. 24 it will be seen that on heating cobalt glass, an increase in the transmission resulted, except in the extreme red end of the spectrum where there was a continual decrease. This

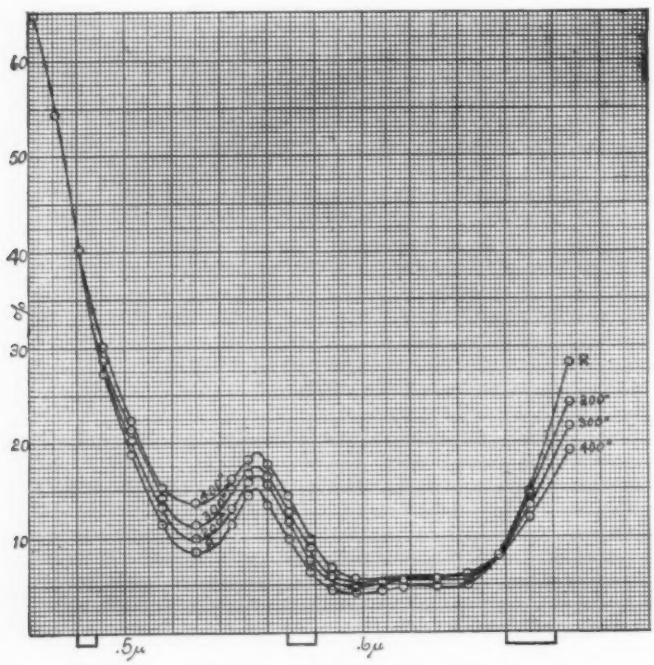


Fig. 24.

Showing percentage transmission of cobalt glass no. 1. Thickness .181 cm.

specimen absorbed considerable light, and consequently rather wide slit widths had to be used in order to measure the light transmitted in the main absorption band. On account of the wide slit width, it is impossible to bring out, very much, the narrow absorption bands, one of which lies in the region .595μ and the other at about .6μ. These are easily discernible with a pocket spectroscope and

with some other arrangement whereby more intense light could be secured, these narrow bands could be defined. On the whole there seems to be a slight general shift of the curve toward the red end of the spectrum. In Fig. 25 is shown the coefficient of absorption for the highest and lowest temperatures measured. If these curves be

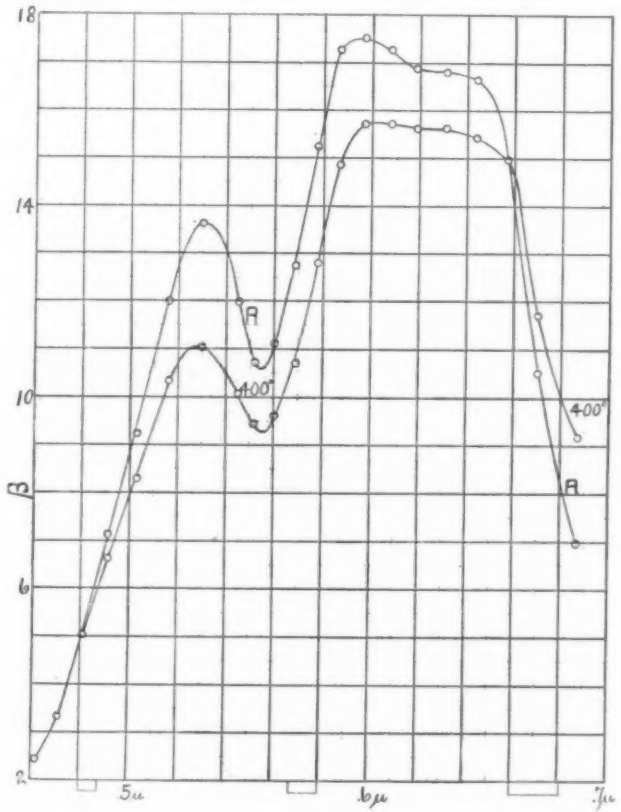


Fig. 25.

Showing the coefficient of absorption of cobalt glass no. 1 at room temperature and at 400°.

compared with the curves shown by Houstoun,[1] it will be found that there is quite a close agreement between the results secured. Houstoun shows by tables and curves in the case of several solids and liquids the values for what he calls the index of absorption

[1]Houstoun, Ann. der Phys., 21, p. 535, 1906.

computed according to a formula due to J. Ehlers. The writer has been unable to make the curves agree exactly with the tables, particularly in the case of the cobalt glass mentioned above.

COBALT GLASS NO. 2.

In Fig. 26 is shown the effect of heating on the transmission of another specimen of cobalt glass, and in Fig. 27 is shown the corresponding coefficient of absorption. These curves indicate the

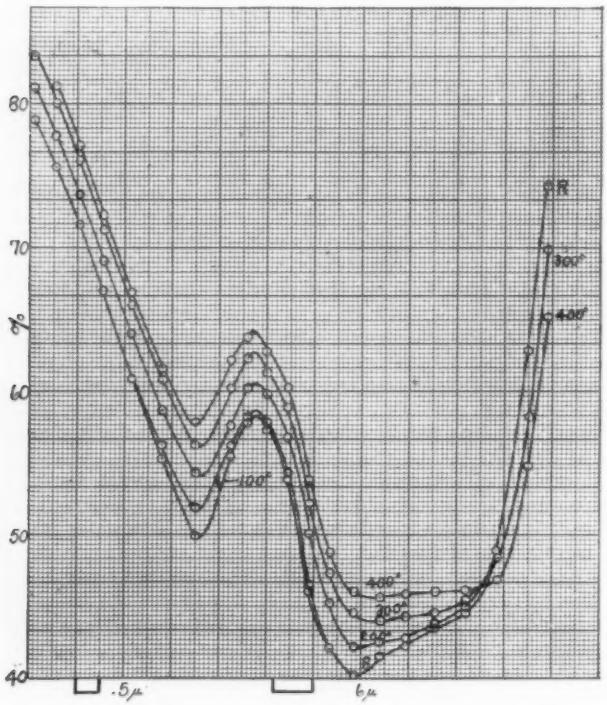


Fig. 26.

Showing the percentage transmission of cobalt glass no. 2 at various temperatures. Thickness = .206 cm.

same effect as was secured with the other specimen of cobalt. A much narrower slit might have been used with this specimen, inasmuch as the absorption was not so large.

GREEN GLASS NO. 1.

From Fig. 28 it can be seen that the transmission of this specimen decreases considerably on heating. There is a considerable shift of

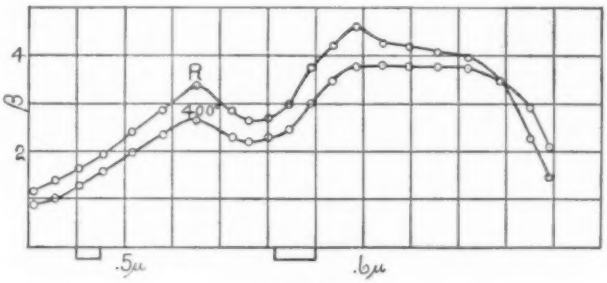


Fig. 27.

Showing coefficient of absorption of cobalt glass no. 2.

the maximum toward the longer wave-lengths, indicating that the absorption band in the violet is either shifting toward the red or is

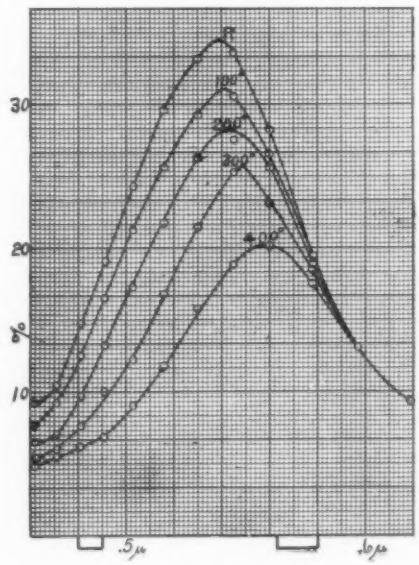


Fig. 28.

Showing the percentage transmission of green glass no. 1 at various temperatures Thickness = .208 cm.

simply becoming broader on that side. Fig. 29 shows the corresponding curves for the coefficient of absorption.

GREEN GLASS NO. 2.

The changes in transmission and coefficient of absorption for green glass no. 2 due to heating are very similar to those mentioned for green glass no. 1, as can be seen by reference to Figs. 30 and 31.

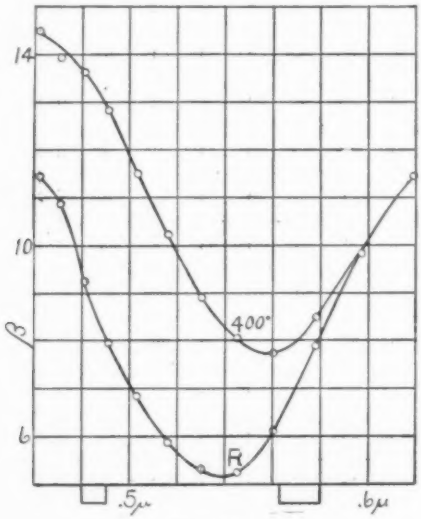


Fig. 29.

Showing coefficient of absorption of green glass no. 1.

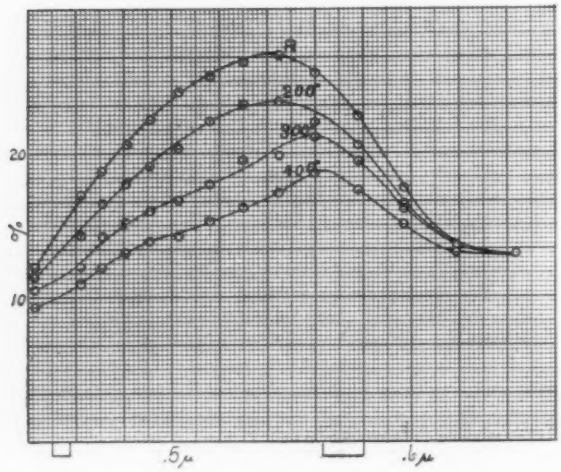


Fig. 30.

Showing percentage transmission of green glass no. 2 at various temperatures. Thickness = .186 cm.

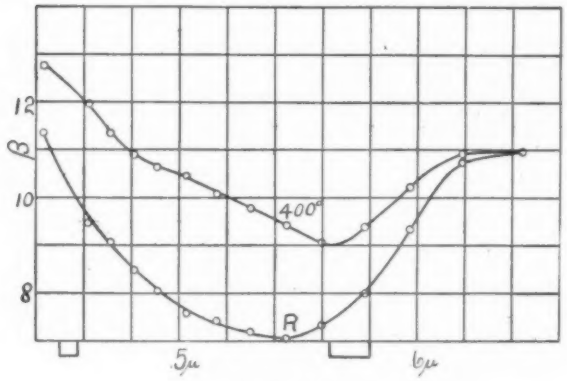


Fig. 31.

Showing coefficient of absorption of green glass no 2.

Blue Glass.

The amount of light transmitted by this glass decreased with rise of temperature as shown in Fig. 32. The absorption was quite

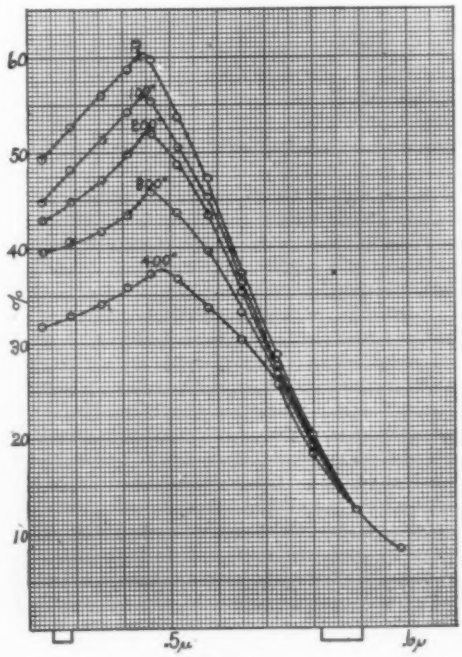


Fig. 32.

Showing percentage transmission of blue glass at various temperatures. Thickness = 226 cm

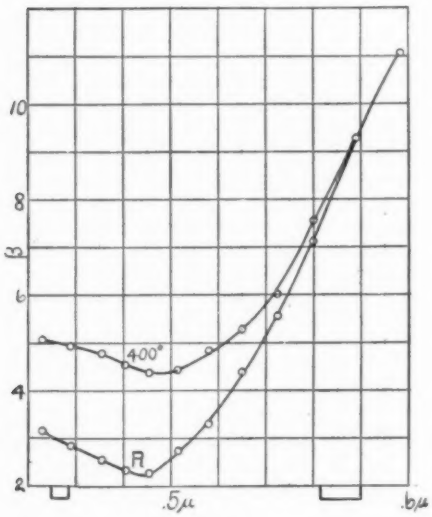


Fig. 33.

Showing coefficient of absorption of blue glass.

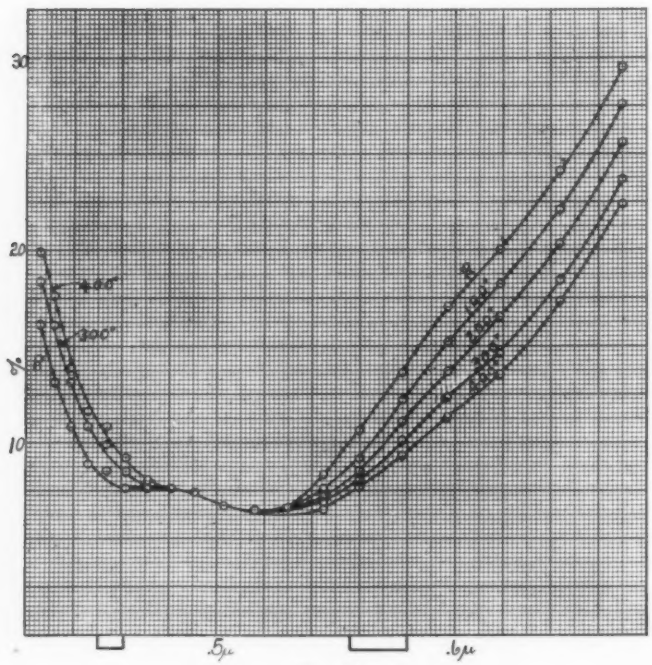


Fig. 34.

Showing percentage transmission of purple glass at various temperatures Thickness = .155 cm.

complete at .6μ, and on heating was very little affected in that region. The maximum for the transmission seems to have shifted slightly toward the longer wave-lengths with increasing temperature and, on the whole, the changes were very similar to those found in the case of the two green glasses. In Fig. 33 are shown the corresponding changes in the coefficient of absorption.

Purple Glass.

On heating the purple glass the transmission for the longer wave-lengths decreased, but increased for the shorter wave-lengths with the result that the absorption band was shifted toward the red.

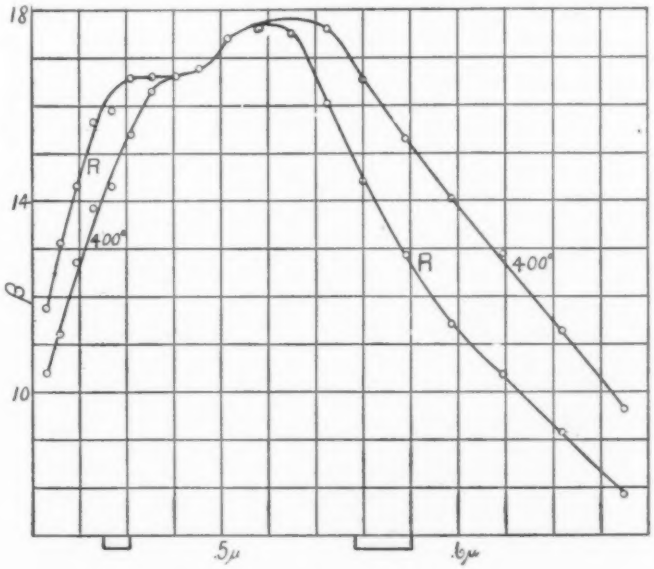


Fig. 35.

Showing coefficient of absorption of purple glass.

In the region of .5μ there was no measurable change. The corresponding changes in the coefficient of absorption are shown in Fig. 35.

Amber Glass.

The curves in Fig. 36 show a gradual increase in the absorption of amber glass with increasing temperatures. The change extends

over the entire range of the spectrum measured, and indicates either a shift of the absorption band toward the red, or what is more likely a broadening of the band on that side. In Fig. 37 are shown the corresponding changes in the coefficient of absorption of amber glass.

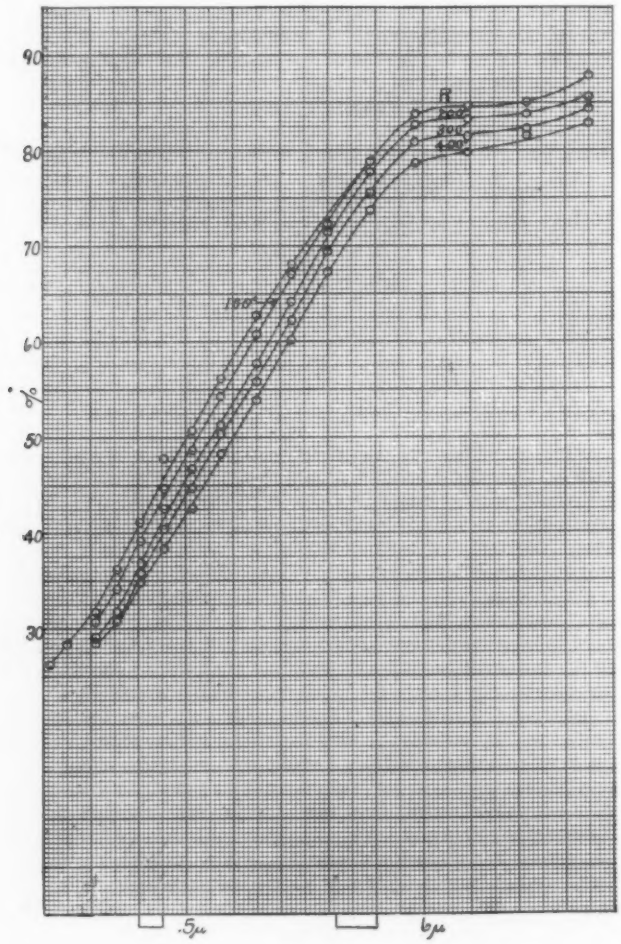


Fig. 36.

Showing percentage transmission of amber glass at various temperatures. Thickness = .155 cm.

URANIUM GLASS.

The curves in Fig. 38 are introduced merely to call attention to a peculiar surface effect which developed on heating and from the

standpoint of changes in the internal absorption they have no meaning. The large changes in the transmission were very surprising

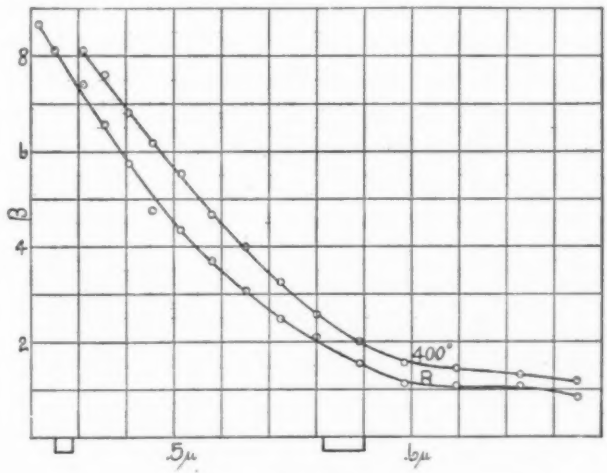


Fig. 37.

Showing coefficient of absorption of amber glass.

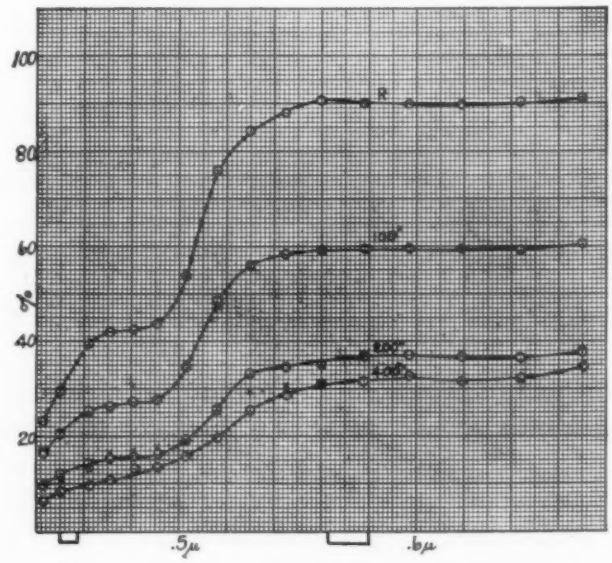


Fig. 38.

Showing percentage transmission of uranium glass at various temperatures with changing surface conditions. Thickness = 1.506 cm.

and, after cooling, another set of observations was made at room temperature, the results of which are indicated by crosses. On removing the specimen from the furnace, the entire surface of the glass was found to be covered with what appeared to be a white powder, but which in reality consisted of small flakes of the glass. These were easily rubbed off, leaving the surface not very unlike that of ground glass. Polishing showed that the effect was entirely a surface one. The exact cause of the flaking has not been determined. The curve marked out by the crosses indicates, in a rough way, that

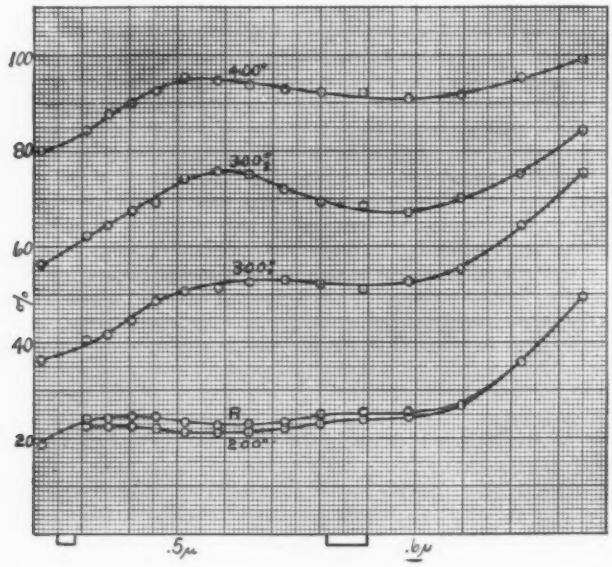


Fig. 39.

Showing percentage transmission of fluorite at various temperatures. Thickness = 1.322 cm.

the internal absorption was increased slightly by heating, although it is not absolutely certain that such is the case. This specimen showed the green flourescence so characteristic of uranium compounds.

FLUORITE.

A cube of fluorite showing purple fluorescence decreased its transmitting power up to about 200° C., and then suddenly began to become more transparent, as shown in Fig. 39. The curve marked

$300°_1$ is the result of observations made very soon after 300° had been reached, the observation being made through the spectrum from blue to red. A few observations were then repeated in the middle of the spectrum, but the settings did not agree at all with those previously made at the same wave-lengths. The transmission was increasing, although the temperature had been uniform for over an hour. Even then the rate of change was so large that one would hardly make a setting and record it before the fields in the telescope would show a contrast. The temperature was kept at 300° and this change watched. The rate of change slowly decreased, and at the end of an hour and a half the intensity had very nearly reached a constant value. Another set of observations was then made through the spectrum with the result shown in curve marked $300°_2$. The fact that the two 300° curves are closer together in the red than in the blue indicates that considerable change occurred while the first observations were being made. The settings for the 400° curve were begun about an hour after reaching that temperature, and at that time the transmission was practically constant. Having become almost perfectly transparent no great amount of further change could be expected. On cooling back to room temperature, the transmission remained practically the same as that shown for 400°. The cube then had been permanently changed from a muddy specimen to a clear one by heating to 400°. Viewing it directly with the eye, one would hardly recognize it as the same specimen. Another fluorite cube had been previously tried, but it broke, due to too rapid heating. The observations, however, had been carried far enough to show that its transmission was changing in a way very similar to the one here described.

Ruby Glass (Surface Film).

A piece of glass covered with a film on one side such that practically only the red of the spectrum is transmitted is called ruby glass. The film of glass no. 1 was thought to contain copper and that of no. 2 gold, and the two specimens may be designated as copper ruby glass and gold ruby glass. In Figs. 40 and 41 are shown the changes in transmission due to the heating of these specimens. The absorption for both specimens increases with rise of temperature

and to about the same extent. On cooling back to room temperature, the intensity of transmission returned to its former values.

Amber Glass (Surface Film).

A piece of glass covered with a film of unknown composition, giving an amber colored transmission spectrum, was also studied at various temperatures with results as indicated in Fig. 42. The absorption, however, decreased on heating, a result which is in direct contrast with the behavior of the ruby specimens. On cooling

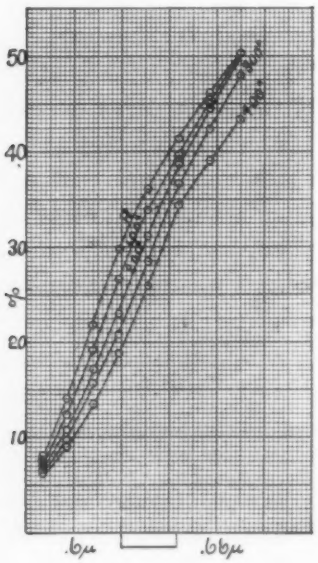


Fig. 40.

Showing the percentage transmission for ruby glass no. 1 at various temperatures.

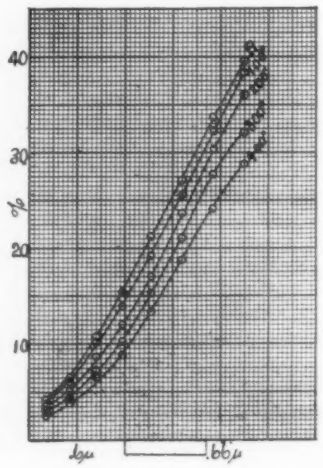


Fig. 41.

Showing the percentage transmission for ruby glass no. 2 at various temperatures.

back to room temperature, the absorption did not quite recover its previous value. A second heating showed again the same changes due to increasing the temperature, and on cooling, a more complete return to the previous room temperature curve.

Theoretical Considerations.

It is generally accepted that absorption of the kind here studied is due to either of two rather closely related though quite distinct

phenomena or a combination of the two. Every substance may be regarded as made up of free electrons and molecules or atoms or groups of atoms with attached electrons, the attached electron together with its atom being commonly called an ion. The relative number of the free and attached electrons varies with the substance,

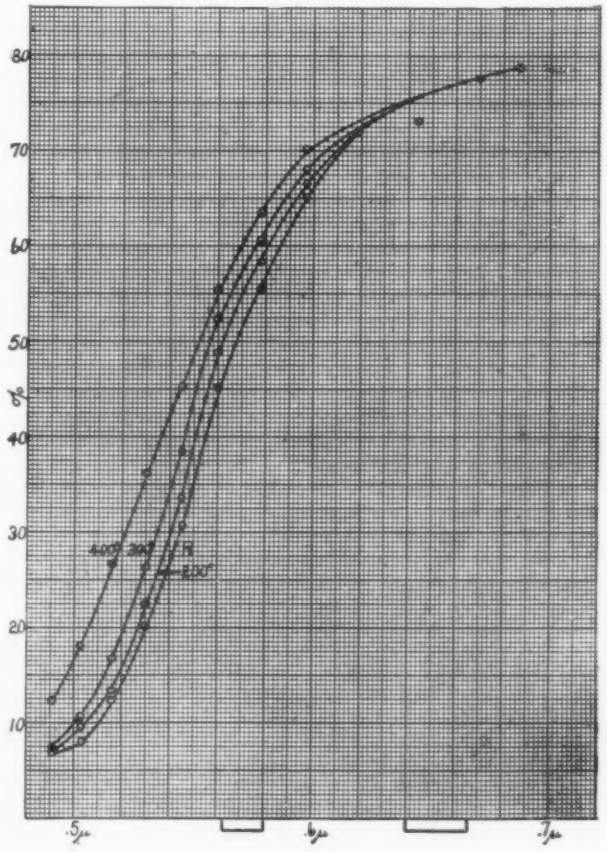


Fig. 42.

Showing percentage transmission of amber glass (surface film) at various temperatures.

and in all likelihood depends on the temperature. A good electrical conductor may be regarded as containing a large number of free electrons, while an insulator has relatively few of these electrons. The free electrons being very light are capable of being set into vibration by disturbances covering a rather wide range of frequen-

cies, whereas the heavy ions can be caused to vibrate only when the conditions for resonance are secured.

The result of increasing the temperature may be and in most cases probably is, to increase the number of free electrons on account of the more violent vibrations of the molecules. But there may be other factors not as yet very well understood which would tend to decrease the number of free electrons on heating. In fact it is not at all improbable that these factors predominate in some substances, over certain ranges of temperature at least, and that in consequence some substances become more transparent as the temperature is raised.

The shifting of absorption bands to different wave-lengths as the result of heating may be accounted for by assuming that the groups of ions break up into simpler groups with slightly different natural periods of vibration. These simpler groups of ions may again combine forming still other groups. The natural frequency of the newly formed groups may be higher or lower than that of the original group, and the absorption band is accordingly shifted toward the shorter or longer wave-lengths.

Summary.

The essential results of these observations taken as a whole may be briefly stated as follows:

1. Heating sometimes increases the absorption and sometimes decreases it. Although the former may occur in the majority of cases, yet the existence of the latter has been amply proven.

2. The selective absorption bands are shifted by heating in some cases toward the longer wave-lengths but in others toward the shorter wave-lengths. The latter phenomena has not, to the knowledge of the writer, been noted by other investigators.

3. In the case of certain specimens a permanent change in the absorption has been found.

The writer hopes to investigate in the near future the effect of low temperatures on the absorption of these same specimens.

The author wishes to acknowledge the many helpful suggestions made by Professors Nichols and Merritt in connection with the investigations here described.

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